Ecotoxicity assessment of pesticide use: methodological and modeling advances in LCA the framework.

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By

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The present thesis entitled *Ecotoxicity assessment of pesticide use: methodological and modeling advances in LCA framework*, by Nancy Angela Lucia Peña Valbuena, was carried out at the Institute of Agriculture and Food Research and Technology (IRTA), under the supervision of Dr. Assumpció Antón, from the department of integral management of organic waste (GIRO) at IRTA, and Dr. Peter Fantke from the Department of Management Engineering at the Technical University of Denmark (DTU), and the tutoring of Dr. Xavier Gabarrell, from the Institute of Environmental Sciences and Technology (ICTA) and the Department of Chemical Engineering at the Universitat Autònoma de Barcelona (UAB).

Assumpció Antón Peter Fantke Xavier Gabarrell

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To my parents and my beloved sister,
Because family is not an important thing. It is everything!

To Oscar,
My love and partner in life,
You paint my world with all kinds of colors

You all are my everything!!

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Table of contents

Acronyms and abbreviations

Abbreviations	Definitions
AI	Active ingredient
CAS-RN	Chemical Abstracts Services Registry Number
CF	Characterization factor
CPC	Central Product Classification
DK	Denmark
DOC	Dissolved organic carbon
EC	European Commission
EEA	European Environment Agency
EF	Effect factor
EFSA	European Food Safety Authority
EU	European Union
FAO	Food and Agriculture Organization of the united nations
FF	Fate factor
FU	Functional unit
Fun	Fungicides
GAP	Good Agricultural Practices
Hrb	Herbicides
HWSD	Harmonized World Soil Database
IPM	Integrated Pest Management
Ins	Insecticides
IS	Impact score
LAI	Leaf area index
LCA	Life cycle assessment
LCI	Life cycle inventory analysis
LCIA	Life cycle impact assessment
MLRm	Multiple linear regression model
NAP	National actions plan
PAF	Potentially affected fraction of species
Pgr	Plant growth regulators
pKa	Acid dissociation constant
PPP	Plant protection products
SETAC	Society of Environmental Toxicology and Chemistry
SOC	Soil organic carbon
UNEP	United Nations Environment Program
US-EPA	United States Environmental Protection Agency
XF	Exposure factor

Abstract

Pesticides are applied to agricultural fields to protect and control crops from pests, disease and undesired weeds, to increase crop productivity and reduce blemishes, and their global use is substantial. Life Cycle Assessment (LCA) is a standardized methodology that can be applied to assess the environmental performance of different product and systems. In LCA, significant advances associated with the evaluation of the agricultural use of pesticides have been made during the past few years, and several approaches have been developed for taking the impacts of pesticide use on human health and ecosystems into account. However, including toxicity-related impacts for pesticide use in LCA is still associated with methodological limitations. Furthermore, considerations for assessing pesticides are currently affected by significant inconsistencies between the life cycle inventory analysis (LCI) and the impact assessment (LCIA) phases of LCA, and this poses as a practical challenge. This thesis, hence, aims to contribute, within the LCA framework, towards the improvement of consistent quantitative methodologies to assess emission fractions and ecosystem toxicity impacts of pesticide use.

One of the main challenges in LCA for agriculture is modeling pesticide emission fractions for the inventory analysis; there are very different approaches and assumptions to provide emission estimates, leading to inconsistent and non-comparable results. This challenge is addressed by testing the influence of the inventory model choice on the environmental performance profiles of different cropping systems. Furthermore, a simplified estimation routine for pesticide emission fractions is proposed, allowing practitioners to include the agricultural field on the assessment. The delineation between pesticide emission inventory and impact assessment has shown to have considerable influence on the estimation of ecotoxicity impacts; in this regard, this study takes advantage of the latest recommendations for pesticide emission inventory and impact evaluation, to frame a suitable interface for LCI modeling and LCIA characterization avoiding possible temporal overlaps.

Another methodological limitation associated with ecotoxicity impacts of pesticide use is how to account for inorganic fungicides in LCA studies involving agricultural systems. To address this, freshwater ecotoxicity impacts of copper-based fungicides were quantified and compared with the most common synthetic fungicides used against downy mildew on a practical case study. Soil ecotoxicity was characterized for specific soil chemistries and textures. To introduce spatial differentiation (critical aspect to describe the toxic effects of metal-based substances) in the ecotoxicity assessment, 7 European water archetypes and more than 15000 soils in three different application scenarios were evaluated.

To capture the complexity and variability of agricultural practices, while simplifying and facilitating the assessment for pesticide application, a series of archetype scenarios was established. These define specific combinations of pesticide target classes, crops and application methods, intended to estimate global emission fractions of pesticides in LCA. This task was conducted in the frame of the LCA pesticide consensus building effort. Finally, the consensual recommendations for simplification and aggregation across conditions are presented and illustrated with a practical example conducted as part of the present thesis.

Results in this thesis demonstrate the importance of considering pesticide use for ecotoxicity assessment in agricultural production and represents a relevant step towards methodological advances in quantifying pesticide emission fractions and their related potential impacts on ecosystems within the LCA framework. Among important follow-up lines of research, future work should focus on the inclusion of pesticide metabolites in the assessment of toxic impacts, the development of characterization factors to account for soil ecotoxicity and the further inclusion of metal emissions from agricultural practices (e.g., application of pesticides, manure and chemical fertilizers) into LCA.

Resumen

Los pesticidas son sustancias ampliamente utilizados en la agricultura para proteger y controlar los cultivos ante plagas, enfermedades y malas hierbas, y mejorar, por tanto, la productividad y reducir posibles pérdidas en las etapas de cultivo y almacenamiento. En los últimos años, la herramienta de evaluación ambiental, análisis de ciclo de vida (ACV) ha alcanzado avances significativos en cuanto a las estimaciones de impacto causadas por el uso de pesticidas en agricultura. Diversas metodologías se han desarrollado para cuantificar los impactos por el uso de pesticidas en la salud humana, así como en los ecosistemas. Sin embargo, existen todavía diversas limitaciones metodológicas e inconsistencias que dificultan una correcta estimación de sus impactos en ACV.

La inclusión de los impactos de toxicidad de los pesticidas se ve gravemente afectada por importantes inconsistencias entre el análisis de inventario (ICV) y la evaluación de impactos (EICV), lo cual conlleva un reto en ACV para poder evaluar y comparar la aplicación de pesticidas con sistemas agrícolas. Es así como esta tesis busca contribuir, desde el marco del ACV, a la mejora de metodologías cuantitativas para evaluar fracciones de emisiones e impactos en la toxicidad de ecosistemas ocasionados por el uso de pesticidas.

Uno de los principales retos en ACV de sistemas agrícolas, es la modelización de fracciones de emisión de pesticidas para el análisis de inventario. En general, existe una gran diversidad de enfoques y suposiciones para estimar dichas emisiones, las cuales suelen ser inconsistentes y difícilmente comparables entre sí. Este aspecto es abordado en el presente trabajo mediante la evaluación de la influencia del modelo de inventario seleccionado, en el desempeño ambiental de diferentes sistemas de cultivo. Además, se propone una estimación rutinaria simplificada de las fracciones de emisión de pesticidas, permitiendo la inclusión del campo de cultivo en el análisis. El delineamiento entre el inventario de emisiones de pesticidas y la evaluación de impactos han resultado tener una influencia considerable en la estimación de los impactos de ecotoxicidad. En este sentido, este estudio toma en cuenta las más recientes recomendaciones sobre inventarios de emisiones de pesticidas y evaluación de impactos, para enmarcar una interface apropiada para modelar el análisis de inventario, así como para caracterizar la evaluación de impactos evitando posibles superposiciones temporales.

Otra de las limitaciones metodológicas asociadas con impactos de ecotoxicidad provocados por el uso de pesticidas, es la inclusión de fungicidas inorgánicos, principalmente compuestos que incluyen metales dentro del ACV de sistemas agrícolas. Este problema es abordado con la cuantificación de impactos de ecotoxicidad en agua superficial producidos por el uso de fungicidas a base de cobre. Estos, a su vez, son comparados en un caso de estudio puntual, frente a los fungicidas sintéticos más comunes empleados contra mildiu. La ecotoxicidad del suelo fue caracterizada en relación a las características químicas y texturas de estos. Para incorporar diferenciación espacial (uno de los aspectos críticos para describir los efectos tóxicos de sustancias metálicas) en el análisis de ecotoxicidad, se evaluaron tres escenarios de aplicación en siete arquetipos de agua en Europa y considerando más de 15000 suelos.

Dada la complejidad y variabilidad de los potenciales escenarios de aplicación de pesticidas y con el objetivo de simplificar y facilitar su evaluación, se han establecido una serie de escenarios arquetipos. Para ello, se definen combinaciones específicas de tipos de pesticidas, cultivos y métodos de aplicación de modo que sea posible estimar las fracciones de emisión de los componentes activos de los pesticidas a nivel global para el ACV. Esta tarea se desarrolla en el marco del esfuerzo internacional, del consenso para pesticidas. Finalmente, las recomendaciones consensuadas sobre la definición de escenarios se presentan por medio de un ejemplo práctico.

Los resultados de esta tesis demuestran la importancia de considerar el uso de pesticidas en la evaluación de ecotoxicidad para producción agrícola. Además, representan una mejora significativa en cuanto a las metodologías para cuantificar fracciones de emisión de pesticidas, así como en la determinación de los impactos de éstos sobre distintos ecosistemas dentro del marco del ACV. Dentro de las líneas a continuar a partir de esta investigación, se puede considerar la inclusión de metabolitos de pesticidas en la evaluación de impactos de toxicidad. Igualmente, el desarrollo de factores de caracterización para considerar la ecotoxicidad en suelos, y una mejor evaluación de la emisión de metales provenientes de los insumos agrícolas (ej. Fertilizantes orgánicos e inorgánicos).

Resum

Els pesticides són àmpliament utilitzats en l'agricultura per protegir i controlar els cultius front plagues, malalties i males herbes, i millorar, per tant la productivitat i reduir pèrdues en les etapes de cultiu i emmagatzematge. En els últims anys, en les eines d'anàlisi de cicle de vida (ACV) s'han assolit avenços significatius pel que fa a l'avaluació de l'ús de pesticides en agricultura. S'han desenvolupat una gran varietat de metodologies per quantificar els impactes degut a l'ús de pesticides en la salut humana, així com en els ecosistemes circumdants.

La inclusió de impactes de toxicitat degut a l'ús pesticides es troba normalment afectada per importants inconsistències entre l'anàlisi d'inventari (ICV) i l'avaluació d'impactes (EICV), comportant un repte en l'ACV per poder avaluar i comparar l'aplicació de pesticides. És així com aquesta tesi busca contribuir, des del marc de l'ACV, en el desenvolupament de metodologies quantitatives per avaluar fraccions d'emissions i impactes en la toxicitat d'ecosistemes ocasionats per l'ús de pesticides.

Un dels principals reptes en l'ACV de sistemes agrícoles, és el modelatge de fraccions d'emissió de pesticides per a l'anàlisi de l'inventari. En general, existeixen varis enfocaments i suposicions per estimar les emissions, però solen ser poc consistents i difícilment comparables entre sí. s'aborda aquest tema en aquest estudi, tot avaluant la influència del model d'inventari seleccionat, en l'acompliment ambiental de diferents sistemes de cultiu. A més, es proposa una estimació rutinària simplificada per a les fraccions d'emissió de pesticides. Els límits entre l'inventari d'emissions de pesticides i l'avaluació d'impactes han resultat tenir una influència considerable en l'estimació dels impactes d'ecotoxicitat. En aquest sentit, aquest estudi contempla les recomanacions actuals d'inventaris d'emissions de pesticides i d'avaluació d'impactes, per poder emmarcar una interfície apropiada per modelar l'anàlisi d'inventari, i caracteritzar l'avaluació d'impactes evitant possibles superposicions temporals.

Una altra limitació metodològica, en el marc des estudis d'ACV, associada als impactes d'ecotoxicitat provocats per l'ús de pesticides, es troba en l'avaluació dels fungicides inorgànics. Aquest problema és abordat amb la quantificació d'impactes d'ecotoxicitat en aigua superficial produïts per l'ús de fungicides a base de coure. Aquests, a la vegada, són comparats en un cas d'estudi puntual, front els fungicides sintètics més comuns emprats contra el míldiu. L'ecotoxicitat dels sòls es va estudiar en relació a les característiques químiques i estructurals

(textures) d’aquests. Per incorporar la diferenciació espacial (un dels aspectes crítics per descriure els efectes tòxics de substàncies metàl·liques) en l'anàlisi d'ecotoxicitat, es van avaluar tres escenaris d'aplicació en set arquetips d'aigua a Europa considerant més de 15000 sòls.

Donada la complexitat i variabilitat dels potencials escenaris d’aplicació de pesticides i amb l’objectiu de simplificar i facilitar llur avaluació s'han establert escenaris agrícoles típics. Per a això, es defineixen combinacions específiques de tipus de pesticides, cultius i mètodes d'aplicació de manera que sigui possible estimar les fraccions d'emissió dels components actius dels pesticides a nivell global per l'ACV. Aquesta tasca es va desenvolupar en el marc de l'esforç internacional de consens per pesticides. Finalment, les recomanacions consensuades sobre la definició d'escenaris es presenten per mitjà d'un exemple pràctic.

Els resultats d'aquesta tesi demostren la importància de considerar l'ús de pesticides en l'avaluació de l’ecotoxicitat per a producció agrícola. A més, representen una millora significativa pel que fa a les metodologies per quantificar fraccions d'emissió de pesticides, així com en la determinació dels impactes d'aquests sobre diferents ecosistemes dins el marc de l'ACV. Dins de les línies a continuar a partir d'aquesta investigació, es pot considerar la inclusió de metabòlits de pesticides en l'avaluació d'impactes de toxicitat. Igualment, el desenvolupament de factors de caracterització per a considerar l'ecotoxicitat en sòls, i una millor avaluació de l’impacte dels metalls pesants existent en les entrades agrícoles (ex. Fertilitzants orgànics e inorgànics).

Preface

This thesis was developed during the period from January 2015 to July 2018 in compliance with the PhD program in Environmental Sciences and Technology of the *Universitat Autònoma de Barcelona (UAB).* The work was carried out at the Institute of Agriculture and Food Research and Technology (IRTA). This dissertation addresses the agricultural use of pesticides in open-field crop production; it is a contribution to the development of methods to assess emissions and effects (i.e. toxicity) of pesticide active ingredients in ecosystems. In particular, for the quantification and characterization of pesticide emissions and impacts, and to improve new considerations for inorganic (i.e. metal-based) pesticides in the frame of life cycle assessment studies.

Part of the research was conducted during a four-month stay, as a research assistant, in the Collaborative Project for Sustainable Organic Low-Input Dairying – SOLID (December 2015 – March 2016) at the Department of Agroecology, Aarhus University, Viborg (Tjele), Denmark. During this period, the environmental performance of different cropping systems was assessed. More specifically the ecotoxicity evaluation of dairy and bio-refinery production, the development of new characterization factors for several pesticide active ingredients and testing the performance of different LCI methodologies. A second two-month stay (April - May 2016), as a guest PhD candidate, in the quantitative sustainability assessment (QSA) division, of the department of management and engineering, Technical University of Denmark – DTU was completed. During this period, the research activities were concentrated on the adaptation of fate system processes to the acid dissociation constant (pKa) into to the *DynamiCROP* model, and the role of metal-based pesticides in agricultural systems for their inclusion in LCA models. Results from the international period are summarized in first authored and collaborative papers, plus several deliverables and conference communications (below listed in this preface).

This thesis is a synopsis of three research articles covering the major findings, which have been either published or accepted or are in preparation to be submitted in international peer-reviewed journals:

- **Peña, N**., Antón, A., Kamilaris, A., Fantke, P., 2018. Modeling ecotoxicity impacts in vineyard production: Addressing spatial differentiation for copper fungicides. Sci. Total Environ. 616-617, 796–804. doi:10.1016/j.scitotenv.2017.10.243.

- **Peña, N**., Knudsen, M.T., Fantke, P., Anton, A., Hermansen, J.E. Freshwater ecotoxicity assessment of pesticide use in crop production: Testing the influence of modeling choices. *Submitted on April 2018 to Journal of Cleaner Production.*
- **Peña, N**., Antón, A., Fantke, P. Towards a consensus to estimate global emission fractions of pesticides: Definition of application scenarios. *Manuscript in preparation.*

In addition, the work included in the thesis was presented in several oral communications and posters in national and international conferences:

- **Peña, N** and Antón, A. "A new approach for modeling inorganic pesticides: an adaptation of life cycle assessment tools to copper fungicides" 13th HCH & Pesticides Forum, 3-6 November 2015, Zaragoza, Spain. *Oral Presentation.*
- Antón, A. and **Peña, N.** "*Impacte ambiental de la utilització de fungicides cúprics a la vinya*" 3r Simposi de Producció Agrària Ecològica. Viticultura i Enologia ecològica, 25-26 November 2015, Vilafranca del Penedès, Spain. *Oral Presentation.*
- **Peña, N**. and Antón, A. "Is copper fungicide that bad?" 3rd International Symposium on Organic Greenhouse Horticulture, 11-14 April 2016, Izmir, Turkey. *Oral Presentation.*
- **Peña, N**., Antón, A., Fantke, P. "A Consistent Framework for modeling Inorganic Pesticides: Adaptation of Life Cycle Inventory Models to Metal-Base Pesticides" 22nd SETAC Europe LCA Case Study Symposium. 20-22 September 2016 Montpellier, France. *Oral Presentation.*
- **Peña, N**., Fantke, P., Antón, A. Modeling Potential Ecotoxicity Impacts due to Copper Fungicide Use in Vineyards. 10th International Conference on Life Cycle Assessment of Food - LCA Food 2016. 19-21 October 2016, Dublin, Ireland. *Oral presentation*.
- **Peña, N**., Knudsen, M.T, Antón, A., Hermansen, J.E. "Development of Characterization Factors for Pesticides in Feed Production" 10th International Conference on Life Cycle Assessment of Food - LCA Food 2016. 19-21 October 2016, Dublin, Ireland. *Oral presentation*.
- **Peña, N**., Antón, A., Dijkman. T, Grant, T., Fantke, P. "Marco consensuado para la inclusión de los pesticidas en los inventarios de ACV" III simposio Red Española ACV. 04 November 2016. UPV-Valencia, Spain. *Oral presentation*.
- Antón, A. and **Peña, N**. "Environmental Assessment of potential toxicity due to fungicide use in vineyards. Focus on copper compounds" 5th Conferencia Internacional de Viticultura Ecologica, Sostenible y Cambio Climático – EcosostenibleWine2016, 4 November 2016, Vilafranca del Penedès, Spain. *Oral Presentation*.
- **Peña, N**., Knudsen, M.T., Fantke, P., Anton, A., Hermansen, J.E. "Significance of pesticide emission modeling for assessing ecotoxicity impacts of agricultural systems: the case of feed production in Denmark" 11th International Conference on Life Cycle Assessment of Food - LCA Food 2018 / AgriFood Asia 2018. 17-19 October 2018, Bangkok, Thailand. *Accepted for Oral presentation*.
- **Peña, N**., "OLCA-Pest. Consens pel càlcul emissions aplicació pesticides". Comptabilitat ambiental a l'agricultura: bases de dades, modelització, aplicabilitat. Jornada tècnica. 8 June 2018 Barcelona, Spain. *Oral Presentation*.

Furthermore, additional training and knowledge were obtained through collaborations in research projects, articles, book chapters and scientific activities during the PhD process.

Participation in projects:

- **VITIMPACT**, Contribución a la evaluación ambiental de la viticultura: cuantificación y ajustes de los factores de emisión en condiciones mediterráneas. Financially supported by INIA-Spain (RTA2015-00091-00-00).
- Collaborative Project **SOLID** (Sustainable Organic Low-Input Dairying). European Community (EC) financial participation under the Seventh Framework Program FP7-KBBE.2010.1.2-02 (GA No. 266367).
- Operationalizing Life Cycle Assessment of Pesticides **OLCA-Pest** project. Financially supported by ADEME (GA No. 17-03-C0025).

Collaborations in articles and book chapters:

- Knudsen, M.T., Dorca-Preda, T., Djomo, S.N., **Peña, N**., Padel, S., Smith, L., Zollitsch, W., Hörtenhuber, S., Hermansen, J.E. The importance of including soil carbon changes, ecotoxicity and biodiversity impacts in environmental life cycle assessment of organic and conventional milk in Western Europe. *Accepted for publication in May 2018 to Journal of Cleaner Production.*
- Parajuli, R., Kristensen, I.S., Knudsen, M.T., Mogensen, L., Corona, A., Birkved, M., **Peña, N**., Graversgaard, M., Dalgaard, T., 2017. Environmental life cycle assessments of producing maize, grass-clover, ryegrass and winter wheat straw for biorefinery. J. Clean. Prod. 142, 3859–3871. doi:10.1016/j.jclepro.2016.10.076
- Sanjuán, N., Fenollosa, L., **Peña, N.,** Escobar, N. LCA as a tool to boost food security. Case study on rice production in Senegal. *Submitted to the International Journal of LCA.*
- Antón, A., Meier, M., **Peña, N**., 2016. Life Cycle Assessment (LCA) and Social Life Cycle Assessment (S-LCA), in Sustainability Assessment Tools for Organic Greenhouse Horticulture. BioGreenhouse COST Action FA 1105, www.biogreenhouse.org. doi:dx.doi.org/10.18174/373584
- Antón, A., Montemayor, E., **Peña, N.**, 2018. “Assessing the environmental impact of greenhouse cultivation”. Chapter 18. In: Achieving sustainable greenhouse cultivation. Leo Marcelis and Ed Hevvelink (Ed) Burleigh Dodds science publishing Limited. Cambridge, United Kingdom.

This thesis is organized into five chapters, with the main contents summarized below. For clarity, the structure of the doctoral thesis is outlined in Figure P.1.

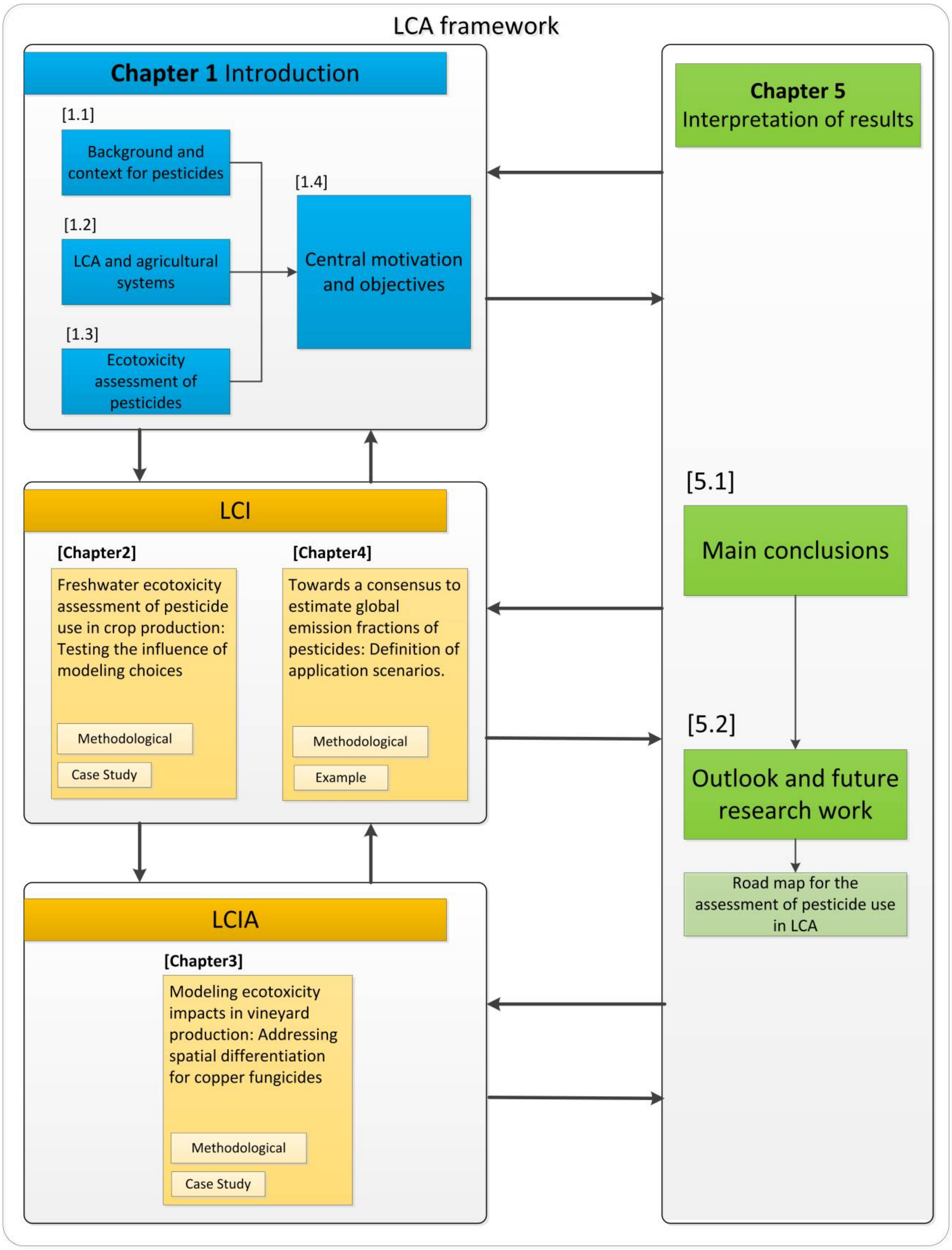

Figure P.1 Structure of the dissertation within the LCA framework

The introduction, background and context for this thesis are set up in **Chapter 1**, stating the problem associated to the current practice for ecotoxicity assessment of pesticide use in agricultural production and defining the needs and objectives of this research study.

Chapter 2 frames a suitable interface for pesticide emission inventory and impact characterization, and the related mass distribution of pesticides avoiding a temporal overlapping. In the same chapter, an estimation routine for pesticide emission fractions is proposed. Furthermore, the influence of pesticide use on the environmental impact profiles of the feed crops maize, grass, wheat, barley, rapeseed and peas, is evaluated testing the effects of the inventory model choice and the developments of the USEtox characterization method.

Chapter 3 improves the considerations for modeling metal-based fungicides in LCA context. First, characterizing fungicide emissions fractions and freshwater ecotoxicity impacts to compare results of copper-based fungicides with the most common synthetic fungicides used. Second, introducing soil ecotoxicity characterization for copper-based fungicides. And finally, including geographic variability for copper-based fungicides used in European vineyards, with the truly dissolved metal fraction evaluated in seven European water archetypes and assessing the potential soil ecotoxicity impacts in different application scenarios for specific non-calcareous vineyard soils.

The key outcomes of the international effort carried out to reach agreement on recommended default agricultural pesticide emission fractions to environmental media are briefly presented in **chapter 4**. A set of typical agricultural scenarios (archetypes for pesticides, crops, application methods and mass fractions) are then defined. Part of the findings of this effort is summarized, and the results related to the definition of application scenarios are presented.

Finally, overall conclusions of the present study along with recommendations for future research work are summarized in **chapter 5**.

Chapter 1.

Introduction

1.1 Background and context for pesticides use

A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest (European Commission, 2009). Agricultural pesticides or plant protection products (PPP) are then those chemicals that are used by farmers to prevent the effects of the pests on the growth and productivity of crops. The end-use products contain one or several active ingredients (AI) and formulants[1]. A wide variety of pesticides can be applied in agriculture and their characteristics depend on a range of factors: including the specific pest (*e.g.*, fungicides, insecticides, molluscicides) and/or plant organism (*e.g.*, herbicides, algaecides and plant growth regulators) of interest; the nature of the AI (synthetic[2] or inorganic) and the mode of action (broad or narrow spectrum) among many others.

Pesticides have become vital elements in modern agriculture as they provide many benefits, but their extensive and continuous applications also have several negative implications for the environment. Some of these implications include human exposure to crop residues (Fantke et al., 2012), potential impacts on non-target organisms (Felsot et al., 2010), a shift in dominating pest species and increasing pest resistance (Pimentel, 2005). Furthermore, climate change is also affecting agricultural production in many ways, increasing pest events, and intensifying the sensitivity of crops to stress and disease (Babut et al., 2013; Kattwinkel et al., 2011). These problems are likely to lead crop growers towards increased use of PPP, and consequently, potential risks of toxic impacts on humans and the ecosystems may further increase (Nesheim et al., 2015; Vernier et al., 2017).

The worldwide consumption of pesticides is about 2 million tons per year. Europe and North America account for 70% of global consumption; from which, 48% are herbicides, 30% are insecticides, and 18% are fungicides (FAOSTAT, 2015). Nowadays, the European Commission

[1] Active ingredient are any chemical, plant extract, pheromone or micro-organism (including viruses), that are the biologically active part in any pesticide, on the other hand the formulant is any substance or group of substances other than the active ingredient that is intentionally added to a pest control product to improve its physical characteristics (European Commission, 2017).

[2] The terms synthetic pesticides and synthetic fungicides in this thesis refer to pesticides that contain xenobiotic organic compounds as active ingredients that are prohibited in organic crop and livestock production (European Commission, 2008).

authorizes more than 500 AI, and around 380000 tons of pesticides are used each year in Europe, from which fungicides represent the most used AI in conventional and organic agriculture, with a total annual use in the EU28 of 163500 tons for 2015 (European Commission, 2009; Eurostat, 2016). Five countries account for nearly 72% of the total pesticide used in Europe for 2015, Spain alone accounts for 20%, followed by France (19%), Italy (16%), Germany (12%) and Poland (5.9%) (Eurostat, 2016).

With regard to pesticide use, the EU adopted the directive (2009/128/EC) to promote the sustainable use of pesticides with the objective of reducing the risks and impacts on human health and the environment (European Commission, 2009). This initiative was part of the strategies of European environmental policy and goes in line with the commitment to reach the sustainable development goals by 2030. The European strategy for PPP acts in three areas, authorization, use and control of PPP as illustrated in Figure 1.1. At the national level, authorities adapt their laws; and develop the National Action Plans (NAP) with main targets and quantitative objectives to ensure the reduction strategy.

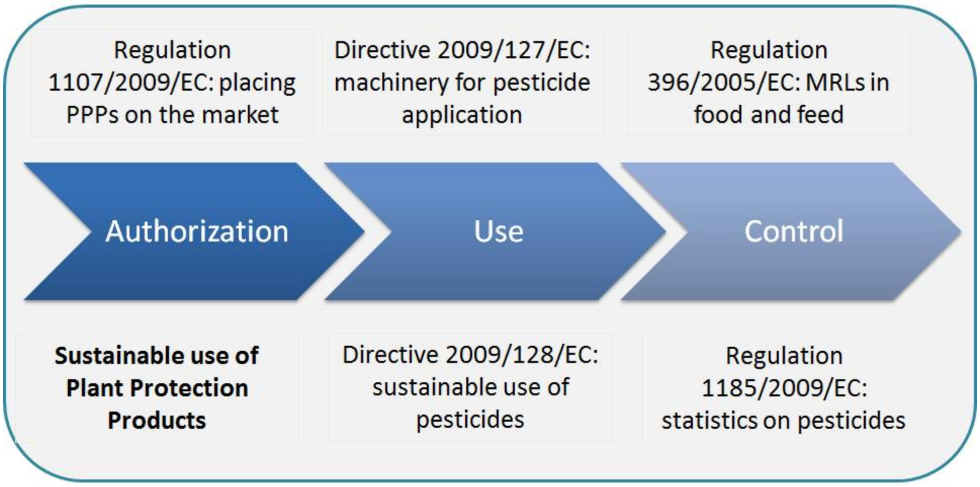

Figure 1.1 European strategies for plant protection products, the pesticide package. Adapted from Rossi et al., (2012)

In line with this regulation, in 2007 the European Commission set out the principles, aims and rules of organic farming (Council Regulation (EC) No. 834/2007). Organic production should respect natural systems and cycles. Biological and mechanical production processes and land-related production should be used to achieve sustainability. Furthermore, the use of pesticides is restricted to inorganic pesticides and exceptionally, synthetic inputs may be permissible if there are no suitable alternatives.

Inorganic pesticides[3] are mainly copper-based products, or in a minor extent, zinc and mercury compounds. On the other hand, zinc and copper are two of the most common heavy metals released from pesticides, accounting for at least ten of the total metals in agriculture. About 80% of the copper contribution to the environment from agricultural systems is from fungicides with active substances derived from copper variants. In this sense, this thesis addresses inorganic pesticides taking as a starting point copper-based fungicides AI.

Finally, aside from their beneficial effects on the crop growth and yield, the use of pesticides is a matter of continuous surveillance and concern, due to potential toxicity to humans and ecosystems (non-target organisms) during or after application (Damalas and Eleftherohorinos, 2011; Fantke et al., 2012; Rozman, 2015; Swartjes, 2016). Pesticide application is considered one of the primary sources of diffuse pollution, meaning that pesticide AI can interact with the media and can be transported by several processes. These processes are governed by the chemical nature of the AIs, and the characteristics of the surrounding environment (Reichenberger et al., 2007). That is why the presence of an AI does not explain environmental impacts by itself, as for that also distribution and transformation in the environment (fate), contact with humans and ecosystems (exposure) and related potential toxicity (effects) in humans and organisms need to be considered and characterized (Hauschild and Huijbregts, 2015; Rosenbaum et al. 2018).

1.2 Life cycle approach for agricultural systems

Life cycle assessment is a standardized tool to assess potential environmental impacts and resources used throughout a product life cycle, i.e., from raw material, through production and use stages, to waste management (Finnveden et al., 2009; ISO-14040, 2006). In contrast to monitoring assessments (*e.g.*, risk assessment), LCA is not used to analyze risk or safety but instead supports to establish and inform environmental performance profiles aiming to identify the most environmentally sustainable ways of providing a product or service between different options.

[3] Here after and throughout this thesis, the term inorganic pesticides are referred to all metal-based pesticides.

In LCA, environmental problems are associated with impact categories to determine the magnitude of potential impacts, by identifying and quantifying the materials and energy flows (including extraction, consumption and emissions) and therefore their potential environmental effects.

LCA is a comparative methodology divided into four phases. The first phase defines the goal and scope of the study; this phase also defines the choice of the functional unit (FU), which must be precise and measurable. This is followed by the inventory analysis (LCI), were all inputs and outputs of the different process involved in the life cycle are listed and quantified for the FU. The third phase, the impact assessment (LCIA) is the stage where the inventoried results are converted into environmental impacts through characterization factors (CF), these impacts are determined eventually for three different areas of protection (Human health, ecosystems quality and resources). In this thesis, only impacts on ecosystems (impact category related to ecosystem quality) are considered (see Figure 1.2).

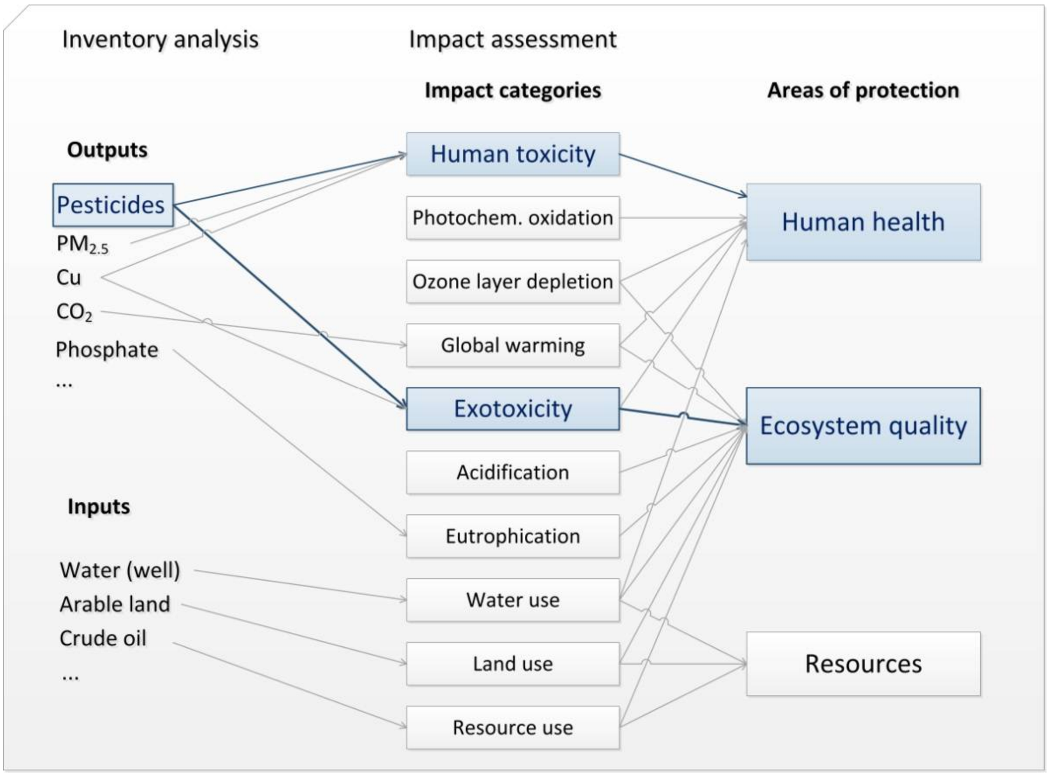

Figure 1.2 Overall scheme of the LCIA framework, linking life cycle inventory output to impact assessment. Adapted from Fantke, (2015)

Interpretation of quantitative and qualitative results is the last phase of an LCA; it allows identifying the potential "hot-spots" of the system under study, and drawn recommendations from the outcomes. The interpretation is correspondingly a critical review of the data quality and the limitations of the analysis may also involve an iterative process within the four phases for revising the scope of the LCA. This technical framework has been established and standardized by ISO (ISO-14040, 2006; ISO-14044, 2006).

LCA has proven to be an accurate, objective and transparent tool to quantify environmental impacts for several types of products and systems. Within the agricultural sector, many cropping systems (Chobtang et al., 2017; Dijkman et al., 2017; Torrellas et al., 2012) and agricultural products (Bartocci et al., 2017; Knudsen et al., 2010; Roy et al., 2009) have been analyzed using LCA framework. However, agriculture is one of the most challenging sectors to study in LCA, since environmental assessment in agriculture has the particularity that the activity has a multifunctional role and evolves in a complex system close to the environment, which is only partly understood (Notarnicola et al., 2017).

Furthermore, assessing environmental impacts associated with agricultural production in LCA needs to account for unique elements inherent in these production systems. For instance, agricultural production has a strong reliance on natural resources (e.g., land, water, nutrients, soil, and biodiversity), is dependent on temporal and spatial conditions, the process and products are highly variable (site specific) and hence difficult to control (e.g., emissions), they are multi-functional systems with a non-linear relationship of the environmental processes. Consequently, there is a high risk for the assessment to be biased by the reduction of system boundaries, the scenario definition, the choice of the functional unit and the considered impact indicators.

Hence environmental models and data need to be developed or adapted to agriculture, the FU and the boundary between the ecosphere (i.e. environmental system) and technosphere (i.e. the studied system) need to be clearly defined, and the databases and calculation procedures need to be efficient and representative.

Up to now LCA studies in agriculture, have successfully dress the evaluation of the so-called global-impact categories (*e.g.,* climate change) or indicators as carbon footprint; while the integration of relevant impact categories related to toxicity or biodiversity has received relatively little attention (Meier et al., 2015). The following elements of this work provide a better understanding of the methodology for ecotoxicity assessment in LCA of agricultural systems and introduce the developments of different methodologies to assess pesticides use.

1.3 Pesticide ecotoxicity assessment in LCA

Pesticides are designed to have a strong and relatively particular toxic effect on targeted organisms. The biologically active part of a pesticide or the active ingredient (AI) is, in general, more active (i.e. more toxic) towards the target organisms, but it can still cause adverse effects on others. Therefore pesticides are likely to affect a broad range of organisms, whether these organisms are intended to be affected or not, and this may be explained by the different modes of action that an AI can have. However, the problem for ecotoxicity assessments is that these modes of action can often not be differentiated and need to be aggregated to be able to capture an effect on an entire ecosystem.

Toxicity is not the only parameter determining potential ecotoxicity impacts; furthermore, they will depend on different driving factors (the quantity emitted, the mobility and persistence, the exposure paths and bioavailability). In addition, ecotoxicity is very different from other impact categories due to the number of relevant and potentially contributing elementary flows (Hauschild and Huijbregts, 2015).

To calculate ecotoxicity impacts scores (IS) for pesticides the mass applied per FU is derived (from the dose and area treated) to then get the mass emitted (i.e. mass applied multiplied by the emission fraction for each compartment) in the LCI. Then, the obtained emitted mass per FU is multiplied by the impact per emitted mass (i.e. impact characterization in the LCIA) for every emission compartment. Thus to assess the potential ecotoxicity impacts caused by pesticide use in LCA studies requires an accurate estimation of the emission fractions in the inventory phase and a precise characterization in the impact assessment (Rosenbaum et al., 2015).

The current LCI practice to estimate emission fractions to different environmental compartments (e.g., air, water or soil) from the applied amount pesticide, several different (i.e. inconsistent) approaches and assumptions are currently used. For example, the use of standard emission factors (i.e. percentages) of the applied active ingredient emitted to air, soil or water (Audsley et al., 2003; Margni et al., 2002). In this line, the most adopted assumption is that 100% of the applied pesticide is emitted to the agricultural soil (Nemecek and Kagi, 2007). Another example are the LCI databases like the “USDA LCA Digital Commons” where pesticides emissions are inventoried according to data on leaching and runoff or the US field crop LCI database and the “EIQ calculator” that reports release of pesticides to soil and air according to the application method inventoried (Cooper et al., 2013; Eshenaur et al., 2015; NREL, 2016). A final example, is the dynamic model PestLCI 2.0 that estimates pesticide emissions to air, surface water, and groundwater, by modeling primary and secondary distribution processes following field application and employing a local fate modeling (Birkved and Hauschild, 2006; Dijkman et al., 2012). Choosing among these different approaches may have an essential influence on the results of the LCI, and consequently, in the LCIA, this is mainly relevant when different agricultural practices need to be addressed (Fantke et al., 2012b).

On the other hand, characterization modeling in LCIA must be done considering the impact pathway, that is, the environmental mechanism leading from the emission to impact. There are multiple impact pathways for pesticides depending on the impact category that is evaluated. In the case of ecotoxicity, the impact pathway of pesticides consists of four main steps: fate, exposure, effects and severity modeling. LCIA assesses impacts at midpoint or endpoint level and relies on substance-specific CFs, that for toxicity denote the quantitative representation of potential environmental impact per unit emission of a substance (Rosenbaum et al., 2018). However, the potential of a substance to contribute to an impact in many cases depends on the environmental characteristics, which can vary spatially (Owsianiak et al., 2013). As mentioned before, spatial variability is observed for all non-global impact categories and is expected to be relevant for pesticide ecotoxicity, been especially true for inorganic pesticides (Potting and Hauschild, 2006).

All current LCA characterization methods adopt environmental multimedia, multipath way models employing mechanistic cause-effect chains to account for the environmental fate, exposure and effects processes. However, they do not necessarily agree on how these processes need to be modeled, leading to differences in results of LCA studies related to the choice of LCIA method (Hauschild and Huijbregts, 2015). Nevertheless, these models consider processes of a pesticide in air, water and soil, and accurately differentiate between natural and agricultural soil.

Freshwater ecotoxicity can be characterized with most of the available methods, such as the UNEP-SETAC scientific consensus model USEtox that is endorsed by the UNEP-SETAC Life Cycle Initiative (Rosenbaum et al., 2008; Westh et al., 2015). For ecotoxicity, USEtox only accounts for impacts on freshwater ecosystems and currently does not provide CF for terrestrial ecotoxicity impacts on or off the agricultural field. Hence, this thesis will mainly adopt this methodology to assess freshwater ecotoxicity impacts.

On the other hand, metal compounds are consistently assessed as very toxic substances in LCIA, and in general have a higher contribution to ecotoxicity than organic/synthetic compounds, even if the last ones are persistent and bioaccumulative (Gandhi et al., 2011; Huijbregts et al., 2000; Owsianiak, 2013). Characterization approaches for metals are typically based on models developed, either for risk assessment or for organic compounds, which miss several processes (i.e. speciation and its dependent of environmental media, natural occurrence and infinite persistence, and metal essentiality) of significant influence to environmental fate and exposure for metals. Attempts have been made by some authors to overcome these limitations, for example, Gandhi et al. (2010) have developed a method for calculating CF of cationic metals in freshwater ecosystems; Dong et al. (2014) further adapted this method to European conditions. For terrestrial ecotoxicity, Owsianiak et al. (2013) propose a spatially differentiated methodology to assess copper and nickel toxicity in soils. Although, for inorganic pesticides, there is still a lack of agreement on how to assess ecotoxicity-related impacts, and in consequence, these AI are currently not adequately characterized by any existing model (Hauschild and Huijbregts, 2015; Meier et al., 2015).

1.4 Main challenges in the assessment of pesticide use in LCA

Over the past years, a significant number of LCA studies on agricultural systems were conducted; however, inconsistencies in the assessment methodology push practitioners to discard the analysis of ecotoxicity impacts, losing valuable information when it comes to comparing different scenarios of agricultural practices.

Pesticide ecotoxicity as currently modeled may lead to inconsistent results and wrong conclusions in few cases (e.g., comparing conventional and organic farming), mostly due to the lack of agreement and precise definitions on the modeling framework for this impact category (Notarnicola et al., 2017). Furthermore, the inclusion of ecotoxicity in LCA does not necessarily mean that the toxic effects of pesticide use are considered. For instance, some authors report pesticide emissions without the impact characterization (Benedetto, 2013). Others, evaluate ecotoxicity impacts related to pesticide production but do not quantify the impacts from the application of PPP (2016; Point et al., 2012). This fact is more apparent when it comes to the evaluation of inorganic pesticides, approved for organic farming, as these are not as well understood and characterized as synthetic pesticides.

Considerable methodological advances have been currently achieved, but existing LCI and LCIA methods do not sufficiently address or even ignore some mechanisms for pesticides. From which some of the most outstanding modeling issues still are: a) the delimitation between LCI and LCIA (temporally and physically); b) modeling emission fractions at LCI phase, and C) the need for spatially differentiated models in the LCIA, especially regarding inorganic pesticides (Nemecek et al., 2014a; Notarnicola et al., 2017; Rosenbaum et al., 2015).

1.5 Central motivation and objectives

Taking into account the main challenges and background described in the previous sections, this research focuses on the ecotoxicity assessment of pesticides active ingredients in the context of LCA. The main motivation for the methodological improvements are related to the aforementioned subjects and further encouraged by the following facts:

- **As a public claim**: according to Eurobarometer (2012) in the report about the attitudes of European citizens towards the environment, the agricultural pollution by the use of pesticides is 6th (29%) on the ten principal concerns and for 33% of Spanish people is a problem of significant concern.
- **As a regional matter**: In 2015, the countries in which the highest quantities of pesticides were sold were France, Spain, Italy, Germany and Poland, together making up 72 % of the EU's pesticide sales (Eurostat, 2017a).
- **As a response of the political concern**: The EU pesticide package under the Regulation (EC) No 1107/2009 of the European Parliament, there is a firm commitment to increases environmental protection and contribute to adopting more sustainable agricultural production.
- **As a regional commitment**: The European Parliament under the 7th environment action program sets the objective towards sustainable use of PPP. Furthermore, for the year 2020, these products should not have a harmful or undesirable influence on the environment (EU, 2013).

- **As the response of scientific concern**: The European Food Safety Authority (EFSA) displays a data gap for exposure assessment of copper compounds from the agricultural use of fungicides (EFSA, 2013).

Hence, this dissertation is focused on the evaluation of pesticides in open-field crop production; it is a contribution to the development of quantitative methodologies to assess emission fractions and toxicity impacts on ecosystems from pesticide use within an LCA framework. Furthermore, the main goal is to advance in the quantification and characterization of emission fractions and toxic impacts derived from the agricultural use of pesticides and improving new considerations for inorganic pesticides in the frame of LCA studies. To achieve this main objective, the following goals are addressed:

- To contribute to the evaluation of the ecotoxicological burden on ecosystems from pesticide use in different crop production systems.
- To evaluate the influence of different LCI modeling approaches to the assessment of environmental impact profiles of crops.
- To include inorganic pesticides in ecotoxicity impact evaluation of agricultural systems. This comprises i) to characterize freshwater and soil ecotoxicity potentials for copper-based fungicides, and ii) to include spatial differentiation on the assessment of metal-based pesticides.
- To define and propose a consistent set of agricultural scenarios to be able to determine emission estimates for inventory use in LCA studies in a global context.
- To recommend lines of future research for furthering the scientific development and the practical applicability of the methodologies for LCA of agricultural systems

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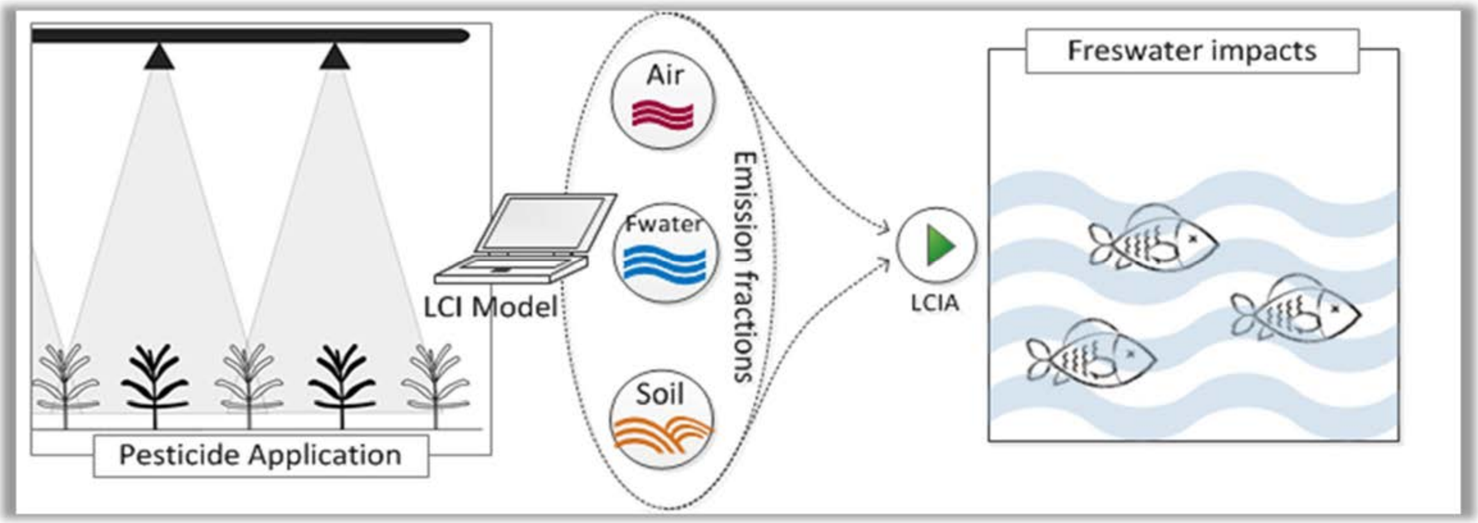

Chapter 2.

Freshwater ecotoxicity assessment of pesticide use in crop production: Testing the influence of modeling choices

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Abstract

Pesticides help to control weeds, pests and diseases contributing, therefore, to food availability. However, pesticide fractions not reaching the intended target may have adverse effects on the environment and the field ecosystems. Modeling pesticide emissions and the alignment with characterizing associated impacts is currently one of the main challenges in Life Cycle Assessment (LCA) of agricultural systems. To address this challenge, this study takes advantage of the latest recommendations for pesticide emission inventory and impact assessment and frames a suitable interface for those LCA stages and the related mass distribution of pesticide avoiding a temporal overlapping. Here, freshwater ecotoxicity impacts in the production of feed crops (maize, grass, winter wheat, spring barley, rapeseed and peas) in Denmark are evaluated during a 3-year period, testing the effects of inventory modeling choice and recent updates of the characterization method (USEtox). Potential freshwater ecotoxicity impacts were calculated in two functional units to consider crop impact profiles and cultivation intensity. According to the results, ecotoxicity impacts decreased over the period, mainly because of the reduction of insecticide active ingredients (*e.g.*, cypermethrine). Three different emission modeling choices were tested; they differ on the underlining assumptions and data requirements. The median results for the resulting emission fractions vary ~4 orders of magnitude for the different models. Main aspects influencing impact results are the interface between inventory estimates and impact assessment, and the consideration of inter-media processes, such as crop growth development and pesticide application method. Statistical differences were found in the impact results with 2 of emission model tested, thereby indicating the influence of modeling choices on ecotoxicity impact assessment.

Keywords Pesticide emission factors - inventory modeling - ecotoxicity characterization -life cycle impact assessment (LCIA) - feed crops - agriculture

2.1 Introduction

With the increased global demand for agricultural products for food, fiber and bioenergy, and the interrelated concerns on the environmental impact hereof, there is a need to have efficient tools to evaluate the environmental performance profiles of agricultural production, to facilitate a move towards more sustainable production systems. LCA is widely applied to quantify potential impacts of products and systems along with their entire life cycles. One of the main challenges in assessing the environmental performance of agricultural systems in LCA is modeling emissions from pesticide use and the subsequent coupling with the impact characterization model (van Zelm et al., 2014). Over the past years, a significant number of LCA studies on agricultural systems were conducted; however, ecotoxicity impacts as currently modeled may lead to inconsistent results and wrong conclusions in few cases (*e.g.*, comparing conventional vs organic farming), mostly due to the lack of agreement and precise definitions on the modeling framework for this impact category (Notarnicola et al., 2017).

The development of the LCI analysis and subsequent LCIA (*e.g.*, pesticide emission quantification and related characterization of ecotoxicity impacts) are the core phases of any LCA study. The robustness and reliability of the LCA results depend mainly on the quality and representativeness of the LCI and LCIA data and models selected. Different modeling options, hence, will affect the impact profiles of a study, and this is especially relevant for agricultural systems (Anton et al., 2014).

Quantifying the chemical emissions to the environment in the LCI phase is typically based on generic assumptions, often based on standard emission factors (*e.g.*, expressed in percentages of applied mass) or dynamic models based on specific application scenarios that describe the emission distribution of organic pesticides. The consensus effort on the delimitation between pesticide emission inventory and impact assessment for LCA already provides guidelines on what should be quantified in those LCA steps but explicitly exclude how to do it avoiding recommendations on specific models (Rosenbaum et al., 2015). The implications of choosing different emission models in the LCA of crop production have been discussed for some agricultural systems (Goglio et al., 2018; Schmidt Rivera et al., 2017; van Zelm et al., 2014). However, no studies are addressing the influence of the pesticide emission modeling approach, nor the evaluation of recent developments in impact assessment methods to determine pesticide ecotoxicity impact profiles in different crop production systems.

Thus, there is a need to test different choices on how to quantify pesticide emission fractions (i.e. different modeling approaches) and the recent developments on the recommended method for freshwater ecotoxicity characterization in the production of feed crops.

The purpose of the present study is to contribute to the evaluation of the ecotoxicological burden on freshwater ecosystems from pesticide use in crop production using the pesticide use in Denmark (DK) as a case of study. It is focused on assessing the influence of pesticides on the environmental impact profiles of feed crops (maize, grass, wheat, barley, rapeseed and peas) during the period 2013-2015, testing the effects of the LCI choice and the developments of LCIA methodology.

This study followed the LCA methodology to evaluate the potential ecotoxicity impacts on freshwater ecosystems from pesticide use in Denmark´s crop production. This bottom-up analysis focuses on the evaluation and influence of pesticide application on the environmental impact profiles of maize, winter wheat, grass, spring barley, rapeseed and peas during the period 2013-2015, testing the effects of the choice of the emission modeling framework and the recent updates of the characterization method. For the later, we use the global consensus model USEtox (http://usetox.org).

2.2 Definition of ecotoxicity impact scores

The quantification of ecotoxicity impact scores for freshwater ecosystems includes 1) detailed LCI reporting on the pesticide AI, application methods, time and mass, location, agricultural practices and crop stage development; 2) quantified AI emission fractions for both on-field and off-field; and 3) measures to avoid double counting of multimedia transfers considered in the quantification of emission fractions and the impact assessment fate modeling (Rosenbaum et al., 2015). Accordingly, the freshwater ecotoxicity impact scores (IS) can be described as:

$$IS = \sum_{i,x} (CF_{i,x} \cdot m_{i,x}) \tag{2.1}$$

Where $CF_{i,x}$ is the characterization factor for freshwater ecotoxicity [PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$], and $m_{i,x}$ is the mass of AI x emitted to compartment i per area treated [$\mathrm{kg}_{\mathrm{emitted}}$ ha^{-1}]. Potential freshwater ecotoxicity impacts (IS_{crop_ha}) [PAF m^3 d ha^{-1}] were determined in relation to 1 hectare [ha] of crop in a given year *t* within 2013 and 2015 (cultivation intensity). Additionally, freshwater ecotoxicity impact profiles at country or regional level (IS_{crop}) [PAF m^3 d $crop^{-1}$] from pesticide use were derived from the product of crop impact scores and the total crop area in a given year in DK.

The interface between LCI and LCIA and related mass distribution for pesticide application in crop production are presented in Figure 2.1. This approach follows the proposed framework for pesticide inventory and impact assessment (Rosenbaum et al., 2015; van Zelm et al., 2014).

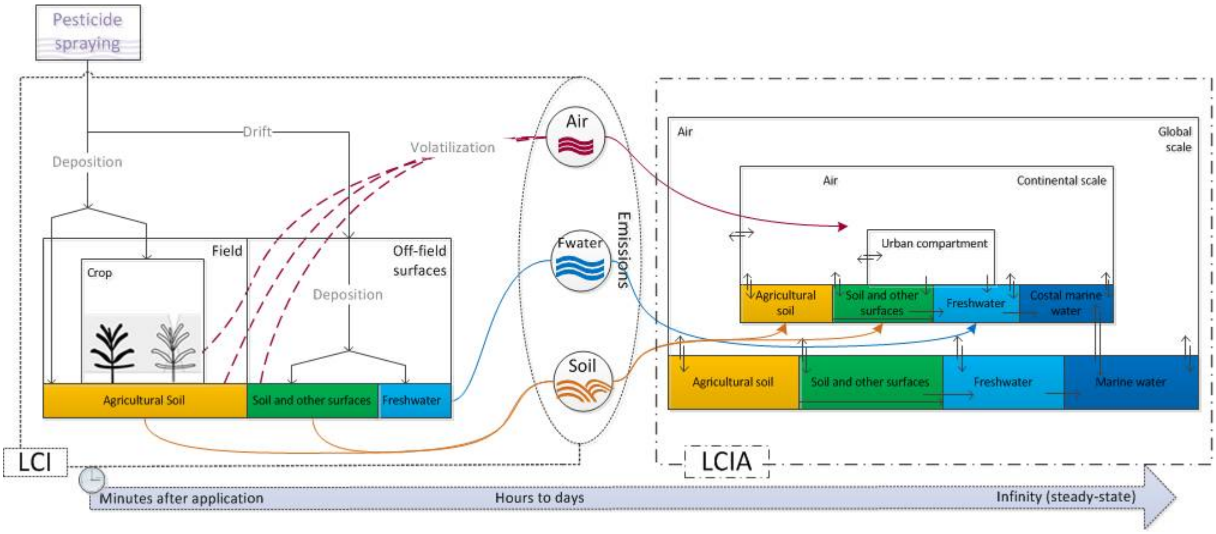

Figure 2.1 Interface between LCI and LCIA for pesticide application in crop production.

2.3 Pesticide emission inventory

Pesticide application practices in DK for the selected crops were determined. Concrete active ingredients were used throughout the study, meaning, that the chemical that is the biologically active part of any pesticide was assessed (European Commission, 2017). The mass applied per AI was derived from the annual statistical report on pesticide use by crop in DK for 2013 (Ørum and Samsøe-Petersen, 2014), 2014 (Ørum and Hossy, 2015) and 2015 (Ørum and Holtze, 2017); for further information see Supporting information for chapter 2 (SI_2-1). We addressed nearly 60 different AIs from four distinct target classes, herbicides (Hrb), plant growth regulators (Pgr), fungicides (Fun), and insecticides (Ins). Additionally, glyphosate (CAS-RN107-83-6) use is not allocated to any specific crop cultivation, and it was assessed as the total agricultural use of the AI per 1 hectare [ha] in a given year, hereafter identified as ($Gly_{\_agri}$).

All AI identification (CAS registry numbers-RN and names), and class are reported in SI_2, Table S2-1.

2.4 Pesticide emission quantification

Crops are treated by foliar spray application (typically boom sprayers), and the reported DK statistics on pesticides were used for agricultural practices. The agricultural field is considered as part of the ecosphere and emissions to environmental media after spraying were modeled via initial distribution (primary processes like initial drift deposition) and secondary emission transfers (*e.g.*, re-volatilization after deposition). The total emission fraction of an AI [kg kg^{-1}] is quantified as the sum of the fractions emitted to air, freshwater and soil:

$$f_{em} = \frac{m_{em}}{m_{app}} = f_{em\_air} + f_{em\_fw} + f_{em\_soil.agri} + f_{em\_soil.other} \quad (2.2)$$

Where f_{em} is the fraction of the applied mass of pesticide that becomes an emission to the environment, m_{em} the mass emitted, m_{app} the mass of pesticide applied, f_{em_air} the fraction of applied mass that is emitted to air, f_{em_fw} the fraction of applied mass that is emitted to freshwater, $f_{em\_soil.agri}$ the fraction of applied mass that is emitted to on-field soil and $f_{em\_soil.other}$ the emission fraction reaching off-field soil and other surfaces.

Primary distribution

The primary distribution processes between compartments occur during the initial minutes after pesticide application. These primary processes are emission by wind drift (f_{d_lost}), pesticide deposition process and the fraction intercepted by the crop or weed. Since the fractions from initial distribution to environmental media should sum up to 100% of the applied mass, considering losses via degradation during the initial minutes negligible, the aggregated emission fractions will be equal to one (Fantke et al., 2011a; Juraske et al., 2007). Consequently, the crop/weed interception fraction (f_{int_crop}) of an AI directly after the application s will be given by:

$$f_{int\_crop} = 1 - \left(f_{d\_lost} + f_{dep\_soil.agri}\right) \quad (2.3)$$

The fraction lost by wind drift f_{d_lost} [kg kg^{-1}], depends on the application method, i.e. the spray equipment and elevation, and wind speed. Based on models for conventional spray equipment on field crops and deposition curve parameters assuming GAP, the f_{d_lost} was fixed to a value of 0.1 (Gil et al., 2014; Gil and Sinfort, 2005; Gyldenkrne et al., 1999; van de Zande et al., 2007). The soil deposition $f_{dep\_soil.agri}$ [kg kg^{-1}], depends on crop-specific leaf area index (LAI), thereby also affecting fractions reaching soil surfaces of the treated field area (Fantke et al., 2011b).

With an exponential model (Gyldenkærne et al., 2000; Juraske et al., 2007), based on crop growth stage and capture efficacy, the fraction reaching the soil surface is described as:

$$f_{dep\_soil.agri} = e^{-k_p \times LAI} \tag{2.4}$$

Where kp is the capture coefficient [-] and set to 0.55 for pesticide spray solutions prepared with adjuvants (Gyldenkrne et al., 1999). Pesticide target class and specific application time were used to define crop-specific growth stages in the selected crops. The LAI was derived for Pgr, Ins and Fun distinctly as a value dependent on the target class/crop growth stage/application time combination, (Fantke et al., 2011b; Itoiz et al., 2012; Olesen and Jensen, 2013); for Hrb application on weeds the corresponding LAI of 0.5 is used. This value is based on the reported leaf cover factor for fallow lands (Panagos et al., 2015). Further details presented in SI_2, Table S2-2.

Secondary distribution

The subsequent secondary emission transfers include re-volatilization after deposition and off-field emissions allocation. The volatilization from fractions deposited in the different compartments is derived from the default Tier 1 emission factors per AI from their vapor pressures (Webb et al., 2016) see Table S2-1 and S2-3 in SI_2-2. The emission factor emF was calculated for each AI (see, SI_2 Table S2-1), the inter-media transfer and the final emission factors are presented in SI_2-1 and SI_2-2. Finally, the water to soil area ratio for DK (0.016) was used to allocate the off-field emissions (i.e. drift fraction deposited in off-field surfaces) see SI_2, Table S2-2. This value is based on reported data of the Danish ministry of environment (Stockmarr and Thomsen, 2009).

2.5 Freshwater ecotoxicity characterization

For assessing the ecotoxicity of pesticides on freshwater ecosystems, we followed the LCIA emission-to-damage framework that links emissions to impacts through environmental fate, exposure and effects (Jolliet et al., 2004). According to (Hauschild and Huijbregts, 2015; Rosenbaum et al., 2008) characterization factors CF for freshwater ecotoxicity of chemical emissions can be expressed as:

$$\mathrm{CF}_{i,x} = FF_{i\rightarrow fw,x} \times XF_{fw,x} \times EF_{fw,x} \tag{2.5}$$

Where $FF_{i\rightarrow fw,x}$ is the fate factor in [d] describing the mass transport, distribution and degradation in the environment. The ecosystem exposure factor, $XF_{fw,x}$, is defined as the bioavailable fraction of a chemical in freshwater; and an effect factor ($EF_{fw,x}$) expressing the ecotoxicological effects in the exposed ecosystems integrated over the exposed water volume. CFs were estimated with USEtox 2.02 as characterization model, with the specific European landscape dataset (i.e. representing DK conditions) (Fantke et al., 2017; Westh et al., 2015). New CFs for 10 additional AIs, following the procedure in Fantke et al. (2017) were derived. A detailed description of the resulting CF and the data used can be found in SI2-3. Furthermore, the recent developments for the characterization model between USEtox versions 1.01 and 2.02 were evaluated.

2.6 Sensitivity analysis

Two types of local sensitivity tests were conducted. First, a scenario sensitivity analysis was performed to test the effect of LCI modeling choices on the impact profile of the selected crops on the three-year period. Three scenarios were considered, the above-described scenario was selected as a reference case (BS) and two alternative scenarios (AS1-AS2) that represent different modeling approaches to quantify emissions from pesticide use. The alternative scenario AS1 followed Margni et al. (2002), which represents a usually used pesticide emission modeling, and furthermore is one of the first approaches that account for pesticide emission distribution in different environmental media in LCA studies for agricultural systems. In this approach, the pesticide emissions are distributed in environmental media based on fixed share percentages. They assume that the fraction of AI emitted to the soil will be 85% of the total application, 5% will stay on leaves and the remaining 10% is lost into the air across crops and pesticides. The second tested scenario AS2 represents fixed emission fractions dependent on the foliar spray application and drift distributions for field crops. This approach was chosen to represent a modeling framework where the initial distribution (i.e. application method and crop relation) is taken into account but also allowing the inclusion of field emissions in the assessment (Balsari et al., 2007; Felsot et al., 2010; Gil and Sinfort, 2005). Table 2.1 displays the emission fractions in the three scenarios considered.

Table 2.1 Comparison of pesticide emission fractions fem calculated by the BS (reference scenario), AS1 (Margni et al. 2002) and AS2 (application method and crop relation).

Emission scenarios	**Average fraction emitted [kg kg^{-1}]**	**Standard deviation on fractions**
BS		
f_{em_air}	1.16x10^{-1}	2.03x10^{-1}
f_{em_fw}	1.60x10^{-3}	0
$f_{em\_soil.agri}$	3.75x10^{-1}	3.11x10^{-1}
$f_{em\_soil.other}$	8.70x10^{-2}	2.01x10^{-2}
AS1		
f_{em_air}	1.00x10^{-1}	0
f_{em_fw}	5.00x10^{-2}	0
f_{em_soil}	8.50x10^{-1}	0
AS2		
f_{em_air}	1.70x10^{-1}	0
f_{em_fw}	1.00x10^{-2}	0
f_{em_soil}	4.50x10^{-1}	0

2.7 Results and discussion

2.7.1 Pesticides use in Danish crop production (2013-2015)

The AI considered in the study covers 98.3% of the total pesticide applications in terms of mass applied for the selected crops: maize, winter wheat, grass, spring barley, rapeseed, peas and the agricultural use of glyphosate ($Gly_{\_agri}$). The total pesticide use was 3165 tons in 2013, 1438 tons in 2014 and 2105 tons in 2015. The average pesticide application rates per crop vary between 2 and 3 orders of magnitude (SI_2, Table S2-6). Grass is the crop with the lowest application rates and pesticide use; together, fungicides and insecticides represent nearly 20% of the total use in grass-2013; additionally, in 2014-2015, there was no use of insecticides, and fungicides use was reduced by less than 2.5%. Gly_agri sum up to 2722 tons in the 3 years and represents near 40% of the total use of pesticides in DK. Winter wheat (2672 tons) is the crop with higher pesticide use followed by spring barley (748 tons) (SI_2, Table S2-7). The most used pesticide target class is Hrb and prosulfocarb is the most used AI after Gly_agri within this target class.

2.7.2 Ecotoxicity impact profiles of feed crops (2013-2015)

The IS_{crop} from pesticide use decreased over the three years (Figure 2.2). The reduction of the IS_{crop} was more apparent in 2014 (59%) than in 2015 (33%) with respect to the base year (2013). Most of the decrease in the IS_{crop} was due to the non-use of a single substance: cypermethrin. This insecticide was the major contributor to IS_{crop} in 2013 across crops (*e.g.,* 87% in maize, 60% in spring barley and 47% in winter wheat) and was no longer used in 2014-2015 (see Table S2-8 in SI_2). Furthermore, the fact that maize and grass did not require the use of insecticides in 2015 also contributes to the reduction of IS_{crop}, but it is essential to note that this may be the result of unfavorable climatic conditions for the emergence of pests, among many other different reasons.

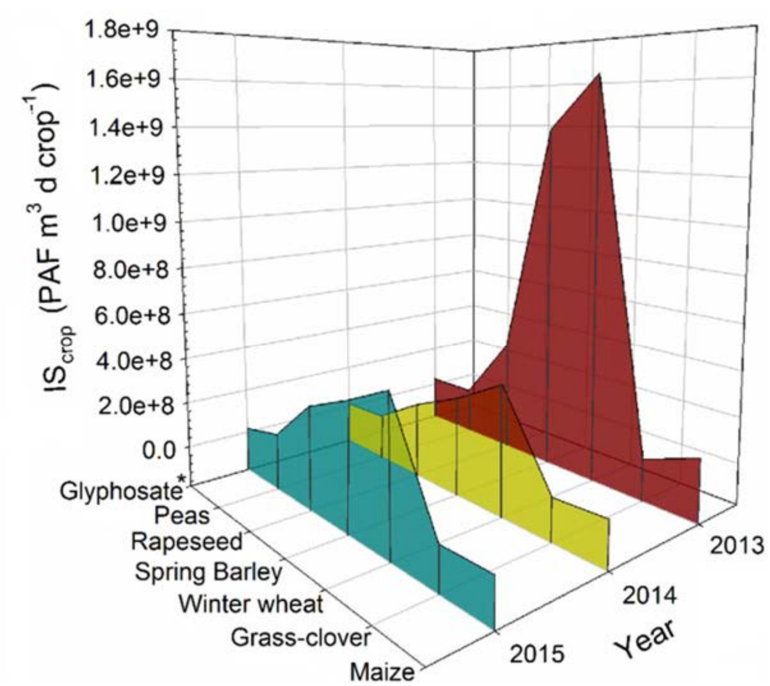

Figure 2.2 Freshwater ecotoxicity impact profiles for crop production (2013-2015), impact scores IS_{crop} in [PAF m^3 d $crop^{-1}$]. *Glyphosate (CAS107-83-6) assessed as the total agricultural use in Denmark

As shown in figure 2.2, winter wheat-2013 ($1.6x10^9$ PAF m^3 d $crop^{-1}$), spring barley-2013 ($1.4x10^9$ PAF m^3 d $crop^{-1}$) and rapeseed-2013 ($3.3x10^8$ PAF m^3 d $crop^{-1}$) present the higher IS_{crop}. The larger IS_{crop} in those crops is associated with the use of Ins (*e.g.,* cypermethrin, pendimethalin and lambda-cyhalothrin) and Fun (*e.g.,* pyraclostrobin, azoxystrobin and folpet), AIs with relatively high CF, and the more extensive cultivation practices (i.e. cultivated area). Consequently, substance prioritization by LCA impact assessment helps to identify potentially harmful AI for ecosystems and, with the restriction of their use or the implementation of more sustainable practices, significant changes in the impact profiles of the crops can be made more apparent (*e.g.*, cypermethrin).

In this sense, if farmers choose to use pesticides AI causing lower impacts, the load on agricultural systems will decline, even if they continue to spray their fields as usual for pests and disease control. Moreover, linking this decision with integrated pest management (IPM) will further contribute to lowering the ecotoxicological burden on freshwater ecosystems from pesticide use.

2.7.3 Pressure of pesticide impacts by hectare and class (2013-2015)

When calculating the potential ecotoxicity impacts on freshwater ecosystems per 1 hectare of crop per year (IS_{crop_ha}) [PAF m^3 d ha^{-1}] the cultivation intensity can be addressed, and thus, their interaction of agricultural systems and practices is more apparent. Different ranking and patterns than the presented in section 2.7.1 are found. Furthermore, the variations in pesticide use (almost 3 orders of magnitude) and impact scores for individual AIs (up to 9 orders of magnitude) are significant. Therefore, in the same year, the two indicators can move in different directions (Figure 2.3), meaning that pesticide use or application rates are not an adequate indicator of potential impacts (*e.g.*, Gly_agri and rapeseed), since toxicity potentials might be higher for pesticides that are applied in lesser amounts (Fantke and Jolliet, 2016).

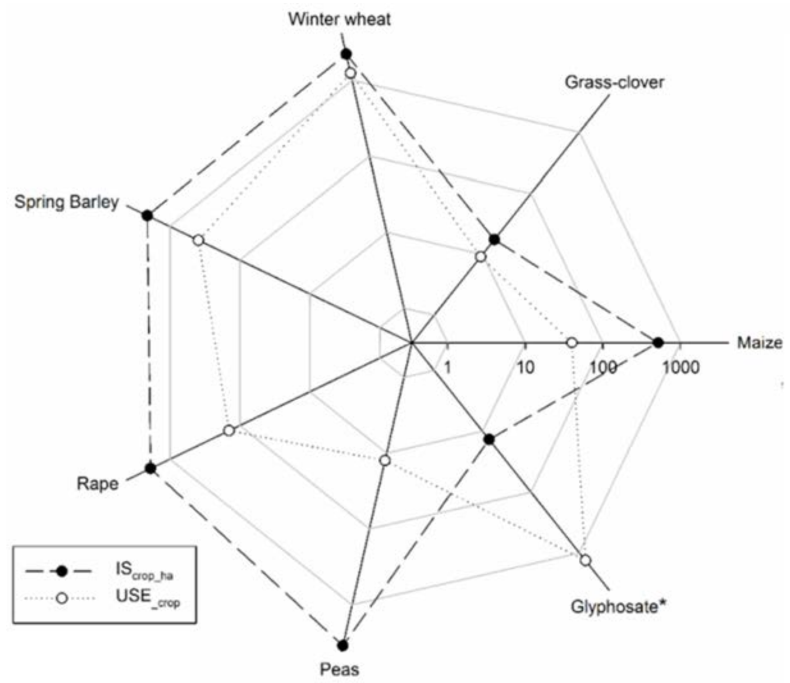

Figure 2.3 Comparison between use of pesticide active ingredient (USE_crop) [tones] and potential freshwater ecotoxicity impacts (IS_{crop_ha}) [PAF m3 d ha^{-1}] for 5 analyzed crops 2013 and *Glyphosate (CAS107-83-6) assessed as the total agricultural use in Denmark in logarithmic scale

In terms of cultivation intensity, peas appeared as the crop with the highest pressure by hectare cultivated in the entire period, with the maximum value (6440 PAF m^3 d ha^{-1}) in 2015. In 2013 rapeseed, spring barley and winter wheat showed IS_{crop_ha} between 64% and 54% lower than peas, in 2014 the difference for the same crops was among 70% and 85% lower and for 2015 all crops showed IS_{crop_ha} 80% lower than peas (see Figure 2.4).

The IS_{crop_ha} for the study varies up to 3.5 orders of magnitude, and the substances cypermethrin (Ins), aclonifen (Hrb), pendimethalin (Hrb) and lambda-cyhalothrin (Ins) present the most significant contribution to IS_{crop_ha}, which his nearly 70% (see Table S2-9).

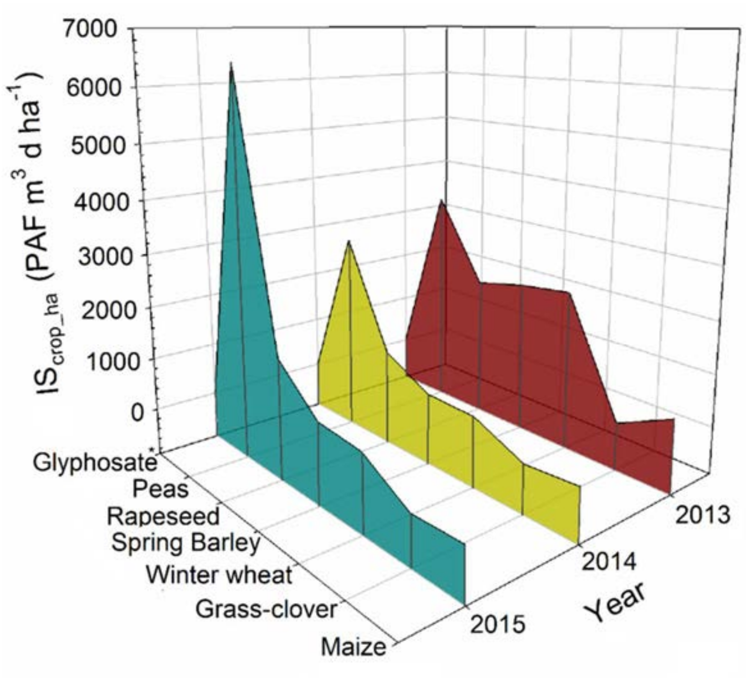

Figure 2.4 Pressure of pesticide impact scores by hectare of crop cultivated for Danish crop production (2013-2015), impact scores IS_{crop_ha} in [PAF m^3 d ha^{-1}]. *Glyphosate (CAS107-83-6) assessed as the total agricultural use in Denmark

The large IS_{crop_ha} for peas-2015, almost double than precedent years, is mainly explained by the bloated use of aclonifen (Hrb). This intensification of herbicide treatments in 2015 could be potentially associated with the emergence of weed infestation in pea's productions fields. Moreover, the sharp increment on IS_{crop_ha} in part is explained by the dose increment by hectare and the relatively high CF for direct emissions to surface water of aclonifen (SI_2, Table S2-5), which is driven by a significant EF ($1.3x10^{+4}$ PAF m^3 kg^{-1}). Furthermore, it is important to note that even if some substances have a high CF; their use could be justified at low doses, because of their agronomic importance and effectiveness of pest or disease control.

The contribution by pesticide target class to freshwater IS_{crop_ha} can be observed in Figure 2.5. Insecticides is the class that contributes in more significant proportion (56%) to impact scores, followed by herbicides (36.4%) and fungicides (7%); plant growth regulators were not included in Figure 2.5 as their contribution to IS_{crop_ha} and IS_{crop_DK} was lower than 1%.

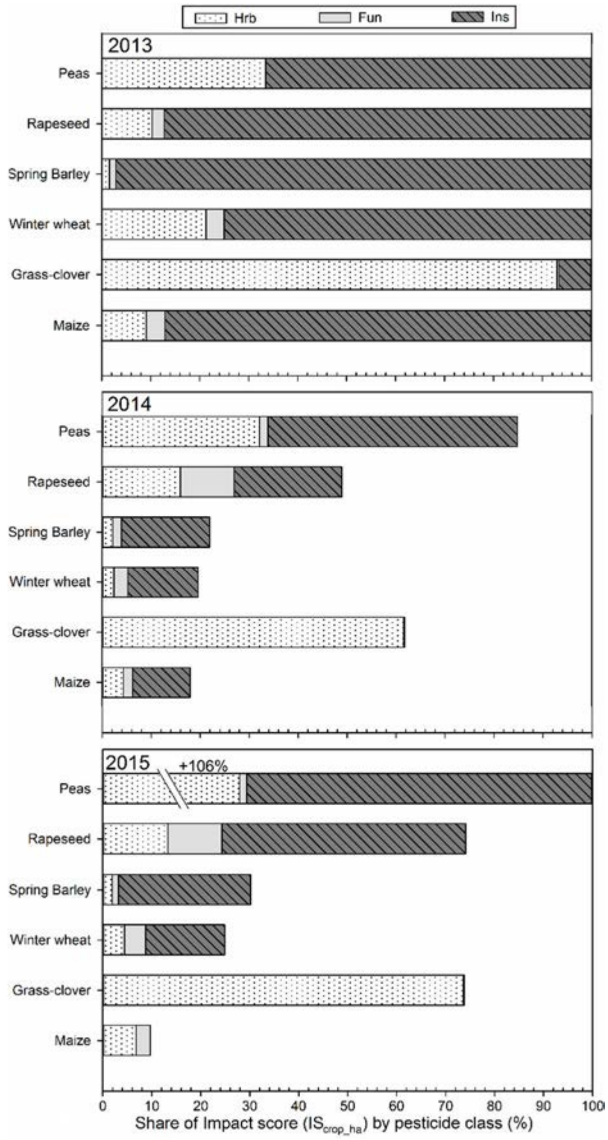

Figure 2.5 Share of freshwater ecotoxicity impact scores IS_{crop_ha} in [%] by pesticide class herbicides (Hrb), insecticides (Ins) and fungicides (Fun) taking as reference per crop IS_{crop_ha} - 2013 as the reference year.

It is well known that pesticide treatments are a highly dynamic activity that varies year by year. Although, it could be more static for herbicides than for the other classes (i.e. insecticides and fungicides) that are more closely correlated with the specific climatic conditions on the area and year of study and thus also the emergence of any specific pest or disease. If these dynamics are to be considered in LCI and LCIA modeling choices, the relevant data (on, *e.g.*, pesticide treatment and crop characteristics) have to be consistently reported (Fantke et al., 2016). As mentioned before IS_{crop_ha} did not follow the same trends of pesticide use, likewise, IS_{crop_ha} did not correlate with use by crop (R^2=0.0006) or by AI.

Similar trends of crop impacts on freshwater ecosystems (unallocated values by hectare and year) are obtained by Nordborg et al. (2014) for the cultivation of maize, rapeseed and winter wheat for biofuel feedstock production; Parajuli et al. 2017 for grass, maize and winter wheat straw for bio-refinery, and Schmidt Rivera et al. 2017 for barley production in Italy and Denmark. The studies above mentioned use PestLCI (version 1 or 2) as inventory model and USEtox 1.01 as characterization method for the impact assessment. Therefore, using a fewer data demanding a simplified approach could lead to the same results for substance prioritization. Despite the similarities in the trends of IS_{crop_ha}, when comparing the results with the absolute values of AI use per 1 ha in a given crop, the IS_{crop_ha} are up to 2.2 orders of magnitude higher; considering the uncertainty range of the characterization method (between 1-2 orders of magnitude) this difference might be moderately significant, and more probably associated with the difference in the LCI and the emission modeling framework.

2.8 Effects of modeling choices on ecotoxicity impact assessment

2.8.1 Comparing the LCI modeling choices

There are very different approaches and assumptions in order to provide emission estimates for quantifying lifecycle emission inventories of pesticides in any LCA study involving agricultural systems. The most simplified approaches are based on generic assumptions regarding varying percentages for pesticide application, the modeling framework of Margni et al., (2002) is used in several agricultural LCA studies. A different approach is the dynamic emission modeling used in PestLCI. This model estimates emissions to three environmental compartments: air, surface water and groundwater. It considers the agricultural field down to 1 m depth into the soil and up 100 m into the air as part of the technosphere, thus excluding emissions to soil on-field and off-field (Birkved and Hauschild, 2006; Dijkman et al., 2012). The main differences between the methods are the underlining assumptions, the definition and alignment between LCI and LCIA and the data requirements for quantifying pesticides emissions. In this sense, modeling approaches that allowed the inclusion of agricultural soil in the assessment and that involve simplified assumptions for at least application methods were selected in order to test the effects on the impact scores from the emission model choice.

The selected methodologies are described in section 2.6, and the results of the three approaches (BS, AS1 and AS2) were compared between the five crops in the 3-year period. The median results for f_{em} in the BS are 2.5 and 1.5 orders of magnitude lower than the emissions for the AS1 and AS2. When modeling f_{em_air} the difference is smaller in comparison with the variations of f_{em_fw} between the three scenarios. Consequently, the variations in the emission fractions lead to further changes in the estimated impact scores.

Results for IS_{crop_ha} in [PAF m^3 d ha^{-1}] with the BS and the AS1 and AS2 are summarized in Table 2.2. BS presented the lowest impact results across all crops and years; the highest impact results appear in AS1, whereas, AS2 showed higher impacts than BS but within 1 order of magnitude of difference. High variability in IS_{crop_ha} results within BS and AS2 approaches were observed.

Table 2.2 Comparison of scenarios to test different emission modeling approaches. Results for potential freshwater ecotoxicity impact scores IS_{crop_ha} in [PAF m3 d ha^{-1}] in the base scenario (BS) and alternative scenarios AS1 and AS2

Crop	BS			AS1			AS2		
	2013	**2014**	**2015**	**2013**	**2014**	**2015**	**2013**	**2014**	**2015**
Maize	513	92	50	14370	2261	582	3041	475	138
Grass	17	11	13	219	141	169	51	31	37
Winter wheat	2210	434	551	58522	11790	14879	12410	2502	3154
Spring Barley	2086	458	631	64214	12888	18305	13514	2701	3808
Rape	1880	921	1394	56586	17682	33144	12244	4144	7267
Peas	3454	2928	6440	110166	69469	120016	23547	14653	26057

In addition, the Tukey test was conducted to determine statistical differences in the impact assessment of the three modeling approaches tested. The differences in results of BS and AS1 are statistically significant. Meanwhile, the results for AS2 and BS were statistically similar.

The delineation between pesticide emission inventory and the impact assessment has shown to have considerable influence on the estimation of ecotoxicity impacts of AI and the impact profiles of crop production (Rosenbaum et al., 2015; van Zelm et al., 2014). However, that alone is not the only explanatory reason for the lower IS_{crop_ha} results. The consideration of inter-media processes, crop growth development and application method allow for a more accurate estimation of the real phenomena, which are also the aspects that usually have the highest influence on LCI and LCIA models (Dijkman et al., 2012; Fantke et al., 2012).

Furthermore, the consistency showed for trend results of others studies using PestLCI (a more sophisticated emission modeling approach) compared to the BS results are satisfactory (see section 2.7.3). Keeping in mind that such a model is much more data demanding and since IS_{crop_ha} represent potential impacts rather than actual damages, the substance prioritization with a simplified method as the BS may serve as a first proxy in LCA studies when more detailed data are lacking.

2.8.2 Variation from LCIA characterization method version

The range of variation for the CF of all AI in the study with USEtox 2.02 was almost 9 orders of magnitude. FF and XF vary by near 2 orders of magnitude, while EF varies up to 7 orders of magnitude indicating substantial differences in pesticide-specific ecotoxicity potential. The variation in the CF for direct emissions to surface water, continental air or agricultural soil was near to 10 orders of magnitude, but CF for direct emissions to continental air and agricultural soil was lower than the CF for direct emissions to freshwater (3 and 2 orders of magnitude, respectively). From which, the importance of modeling the impacts of the dose applied, with a coherent coupling of the LCI to the LCIA model results (i.e. characterized results).

Results for IS_{crop_ha} in the base scenario (BS) and USEtox version 1.0 and 2.02 are summarized in Table 2.3. The more substantial differences in the impact results from both USEtox versions are the AI coverage, with version 1.01 covering fewer AI; thus, IS_{crop_ha} characterized with v 1.0 are lower in most of the cases due to AI coverage, as expected. Furthermore, significant improvements and scientific consensus have been achieved for the new features introduced in the USEtox version 2.02 among which substances and updated substance data and continent-specific landscape parameters contribute to further improving the accuracy in the quantification of CFs. An example of this, are the results for Peas 2013 to 2015, were all IA were included in both USEtox versions, and IS_{crop_ha} were within the same order of magnitude but between 3 to 6 times larger.

Table 2.3 Comparison of scenarios to test developments of LCIA characterization method. Results for potential freshwater ecotoxicity impact scores IS_{crop_ha} in [PAF m3 d ha^{-1}] in the base scenario (BS) and USEtox version 1.0 and 2.02

Crop	BS - USEtox 1.0			BS - USEtox 2.02		
	2013	**2014**	**2015**	**2013**	**2014**	**2015**
Maize	246	63	146	513	92	50
Grass	24	12	14	17	11	13
Winter wheat	1349	445	1223	2210	434	551
Spring Barley	758	267	390	2086	458	631
Rape	776	563	702	1880	921	1394
Peas	1483	1893	6080	3454	2928	6440
Glyphosate Agri-use	24	12	17	14	6	8

2.8.3 Results for the sensitivity analysis

The results on the evaluation of ecotoxicity impact profiles in Danish crop production demonstrate that modeling freshwater ecotoxicity impacts with the BS and USEtox 2.0 allows to recognize trends of different pesticides treatments and burdens on freshwater ecosystems, thus accounting for interactions between different compartments and a defined clear interface between LCI and LCIA (Figure 2.1).

The variations of the emission fractions to air, surface water and soil were 6 orders of magnitude. Given the input parameter sensitivity analysis presented in the Supplementary material SI2-5, the primary sources of uncertainty in the proposed emission modeling framework are identified as i) the application method and the drift fractions, and ii) the allocation for the off-field emission, specifically the water to soil ratio (as shown in figure 2.6). Although, the uncertainty range associated with pesticide emissions have not yet been quantified and is beyond the scope of the present study.

The uncertainty of CFs (USEtox 2.02) due to emissions to air, freshwater and agricultural soil is 176, 18 and 103 GSD^2 (Rosenbaum, 2016). The major sources of uncertainty are substances half-lives and ecotoxicity EF (Henderson et al., 2011). Furthermore, in comparison with the FF and XF, the EF shows a substantial variation among the substances covered in this study, explaining a large part of the variations in the CFs for the AI after emissions to freshwater.

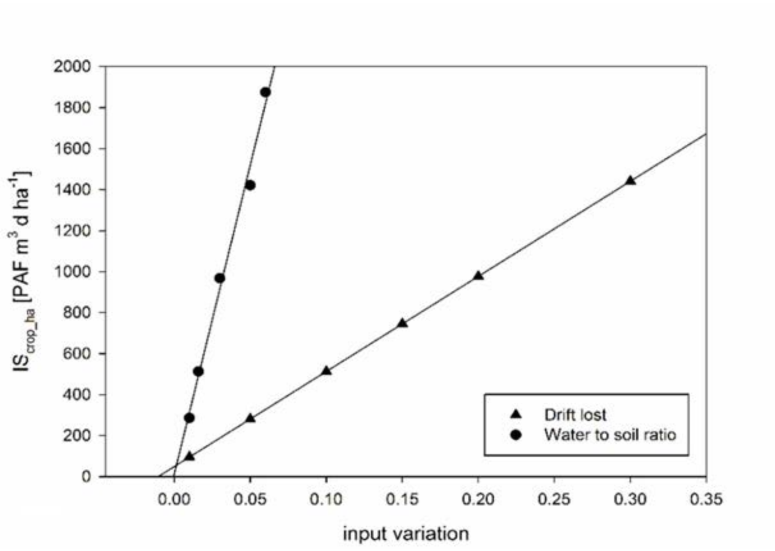

Figure 2.6 Sensitivity to model input parameters of BS. Variation for ecotoxicity impact scores (IScrop_ha) in [PAF m3 d ha^{-1}] of Maize in 2013 (Mz-13).

2.9 Conclusions

LCI modeling options do affect the ecotoxicological burden on freshwater ecosystems from pesticide use, and directly affects substance prioritization in LCA studies. Furthermore, the updated CF with the continent-specific landscape parameters contributes to a broader assessment. In the case of scenario and sensitivity analysis, the main findings identified application method and allocation for the off-field emission, as the main descriptors for modeling emissions of pesticides. The use of the modeling framework presented in this study allows for delivering more robust results and accurate evaluation of ecotoxicity impacts. Finally, to provide consumers and policymakers with more reliable information on the environmental performances of agricultural systems, LCA studies need to include all relevant emission outputs; therefore, a final consensus needs to be reached with a specific emission model recommendation.

Acknowledgments

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Supporting information for chapter 2 (SI_2)

SI2-1 Pesticide active ingredients

The mass applied of pesticide per AI was derived from the annual statistical report on pesticide use for each specific crop in Denmark for 2013 (Ørum and Samsøe-Petersen, 2014), 2014 (Ørum and Hossy, 2015) and 2015 (Ørum and Holtze, 2017). All AI used for industrial applications and the pesticide class “Molluscicide” where excluded from the study.

Table S2-1 lists AI in this study along with their CAS-RN, pesticide classification, vapor pressures [mPa] and the resulting Tier 1 emission factors (emF). The AI not characterized by USEtox version 2.02 where calculated for this study, these AI are marked in the table (†), and further descriptions on the data used for this procedure can be found in section S2-3.

Table S2-1. Evaluated active ingredients, identification (CAS-RN), pesticide class, vapor pressures and Tier 1 emission factors per AI

CAS-RN	Active Ingredient	Class[a]	Vp[b]	emF
25057-89-0	Bentazon	Hrb	1.70×10^{-1}	0.15
69377-81-7	Fluroxypyr	Hrb	3.80×10^{-6}	0.01
173159-57-4	Foramsulfuron †	Hrb	4.20×10^{-9}	0.01
104206-82-8	Mesotrion †	Hrb	5.70×10^{-3}	0.01
40487-42-1	Pendimethalin	Hrb	$3.34 \times 10^{+0}$	0.50
133855-98-8	Epoxiconazol	fun	1.00×10^{-2}	0.01
175013-18-0	Pyraclostrobin †	fun	2.60×10^{-5}	0.01
52315-07-8	Cypermethrin	Ins	6.78×10^{-3}	0.01
94-74-6	MCPA	Hrb	4.00×10^{-1}	0.15
79277-27-3	Thifensulfuron-methyl	Hrb	5.19×10^{-6}	0.01
60207-90-1	Propiconazol	fun	5.60×10^{-2}	0.05
60-51-5	Dimethoat	Ins	2.47×10^{-1}	0.15
94-75-7	2,4-D	Hrb	9.00×10^{-3}	0.01
1689-84-5	Bromoxynil	Hrb	1.20×10^{-1}	0.15
83164-33-4	Diflufenican	Hrb	4.25×10^{-3}	0.01
1689-83-4	Ioxynil	Hrb	2.04×10^{-3}	0.01
52888-80-9	Prosulfocarb	Hrb	7.90×10^{-1}	0.15
105512-06-9	Clodinafop-propargyl	Hrb	3.19×10^{-3}	0.01
71283-80-2	Fenoxaprop-P-Ethyl	Hrb	5.30×10^{-4}	0.01
74223-64-6	Mesosulfuron-methyl	Hrb	1.40×10^{-8}	0.01
141776-32-1	Sulfosulfuron	Hrb	3.05×10^{-5}	0.01
101200-48-0	Tribenuron-methyl	Hrb	5.30×10^{-5}	0.01
999-81-5	Chlormequat-chlorid	Pgr	1.00×10^{-3}	0.01

CAS-RN	Active Ingredient	Classa	Vpb	emF
16672-87-0	Ethephon	Pgr	1.00x10^{+0}	0.15
24307-26-4	Mepiquat-chlorid	Pgr	1.00x10^{-5}	0.01
95266-40-3	Trinexapac-ethyl	Pgr	2.16x10^{+0}	0.50
131860-33-8	Azoxystrobin	fun	1.10x10^{-7}	0.01
188425-85-6	Boscalid †	fun	7.20x10^{-4}	0.01
121552-61-2	Cyprodinil	fun	5.10x10^{-1}	0.15
67306-00-7	Fenopiridin †	fun	1.70x10^{+1}	0.95
125116-23-6	Metconazol †	fun	2.10x10^{-5}	0.01
178928-70-6	Prothioconazol †	fun	4.00x10^{-4}	0.01
107534-96-3	Tebuconazol	fun	1.30x10^{-3}	0.01
67375-30-8	Alpha-cypermethrin	Ins	3.80x10^{-4}	0.01
91465-08-6	Lambda-cyhalothrin	Ins	2.00x10^{-4}	0.01
23103-98-2	Pirimicarb	Ins	4.30x10^{-1}	0.15
102851-06-9	Tau-fluvalinat	Ins	9.00x10^{-7}	0.01
1918-00-9	Dicamba	Hrb	1.67x10^{+0}	0.50
82097-50-5	Triasulfuron	Hrb	2.10x10^{-3}	0.01
81777-89-1	Clomazone	Hrb	1.92x10^{+1}	0.95
1702-17-6	Clopyralid	Hrb	1.36x10^{+0}	0.50
101205-02-1	Cycloxydim	Hrb	1.10x10^{-2}	0.05
2764-72-9	Diquat	Hrb	1.00x10^{-3}	0.01
1918-02-1	Picloram	Hrb	8.00x10^{-5}	0.01
111479-05-1	Propaquizafop	Hrb	4.39x10^{-7}	0.01
23950-58-5	Pronamide	Hrb	5.80x10^{-2}	0.05
173584-44-6	Indoxacarb	Ins	6.00x10^{-3}	0.01
123312-89-0	Pymetrozine	Ins	4.20x10^{-3}	0.01
111988-49-9	Thiacloprid †	Ins	3.00x10^{-7}	0.01
74070-46-5	Aclonifen	Hrb	1.60x10^{-2}	0.05
1071-83-6	Glyphosphate	Hrb	1.31x10^{-2}	0.05
133-07-6	Folpet	fun	2.10x10^{-2}	0.05

[a] Target classes: herbicides (Hrb), fungicides (Fun), insecticides (Ins) and plant growth regulators (Pgr)
[b] Vapor pressure (Vp) for AI in mPa at 25ºC
[c] Tier 1 emission factors per AI (Webb et al., 2016).
† AI with new CF

SI2-2 Pesticide emission quantification

This section describes the equations and data used for the quantification of emissions of AI to air, surface water and soil for the different crops in the three-year period.

Table S2-2. Transfer processes considered for pesticide emission quantification in both primary and secondary emission transfers

Transfer processes	Formulation
Fraction lost by wind drift	$f_{d\_lost} = 0.1$
Deposition processes	
Soil deposition	$f_{dep\_soil} = e^{-k_p \times LAI}$
Leaf deposition	$f_{dep\_leaf} = 1 - e^{-k_p \times LAI}$
Volatilization processes	
Volatilization from Leaf deposition	$f_{vol \leftarrow leaf} = f_{dep\_leaaf} \cdot emF$
Volatilization from fraction deposited on-field soil	$f_{vol \leftarrow soil.agri} = f_{dep\_soil} \cdot emF$
Volatilization from fraction deposited on off-field soil	$f_{vol \leftarrow soil.other} = f_{dep\_soil} \cdot emF$
Off-field emissions allocation	
fraction allocated to freshwater	$f_{all\_fw} = f_{d\ lost} \cdot \left({}^{sw}/_{soil} \right)$
fraction allocated to off-field soil	$f_{all\_soil.other} = f_{d\ lost} - f_{em\_sw}$

Note: LAI [$m^2\ m^{-2}$], leaf area index, Kp [-], substance capture coefficient. Indices dep, vol, emF, d_los denote processes deposition, volatilization, tier 1 emission factor, drift lost; sw, agri_soil denote compartments surface water, agricultural soil; and *f* stands for fraction. The term (sw $soil^{-1}$) represents the water to soil ratio in Denmark.

Table S2-3. Default Tier 1 emission factors (emF) per AI from their vapor pressures (Webb et al., 2016)

Vapor pressure class	Vapor pressure (mPa)	emF
Very High	Vp > 10	0.95
High	1 < Vp < 10	0.50
Average	0.1 < Vp < 1	0.15
Low	0.01 < Vp < 0.1	0.05
Very low	Vp < 0.01	0.01

SI2-3 Characterization factors for pesticide AI

CFs for some of the AI collected in the LCI (see Table S2-5) were not available in USEtox 2.02. The new CFs were calculated following the recommendations of USEtox procedures (Fantke et al., 2017). The physicochemical and toxicological effect data were collected, adapted or derived from primary and secondary data sources (summarized in Table S2-3), imported into the organic substances database to finally be able to calculate the CF for the new imported substances.

Table S2-4. Primary and secondary data sources for calculation of CFs with USEtox 2.02

Parameter	Symbol	Unit	Sources	
			Primary	Secondary
Chemical abstract	CAS-RN	-	PPDB [a]	ChemSpide[e]
Target Class	-	-	PPDB	ChemSpider
Molecular weight	MW	G mol^{-1}	PPDB	ChemSpider
Pesticide ChemClass	pKa	-	TOXNET [b]	EPI Suite
Dissociation constant (pKa at 25oC)	pKa.gain	-	TOXNET	EPI Suite
	pKa.loss	-	TOXNET	EPI Suite
Octanol-water partition coefficient	KOW	L L-1	PPDB	EPI Suite
	KOW	Log P	PPDB	EPI Suite
Org. Carbon-water partition coefficient	Koc	L kg^{-1}	QSAR (estimation)	EPI Suite
Henry law coefficient (at 25˚C)	KH25C	$Pa.m^3.mol^{-1}$	PPDB	EPI Suite
Vapor pressure (at 25˚C)	Pvap25	Pa	PPDB	EPI Suite
Solubility - In water (at 25˚C)	Sol25	Mg L^{-1}	PPDB	EPI Suite
Partitioning coefficient between dissolved and organic carbon‡	Kdoc	L kg^{-1}	Calculated	-
Degradation rate in air	kdegA	s^{-1}	EPI Suite [c]	Calculated‡
Degradation rate in water	kdegW	s^{-1}	EPI Suite	Calculated‡
Degradation rate in sediment	kdegSd	s^{-1}	EPI Suite	Calculated‡
Degradation rate in soil	kdegSl	s^{-1}	EPI Suite	Calculated‡
Generic (average) plant. diss	kdissP	s^{-1}	Fantke et al., 2014	-
Species-specific eco-toxicity data	avlogEC50	Mg L^{-1}	ECOTOX DB [d]/TOXNET	-
Bioaccumulation factor in fish	BAFfish	L $kgfish^{-1}$	Experimental data	EPI Suite

[a] (Lewis et al., 2016), [b] (US National Library of medicine, 1993), [c] Estimation Program Interphase (EPI) Suite TM version 4.11 (US Environmental Protection Agency, 2012), [d] (EPA, 2016), [e] (Royal Society of Chemistry, 2015). ‡ For specifications on how to calculate these parameters please refer to (Fantke et al., 2017).

Characterization Factors estimated with USEtox 2.02, with the specific European landscape dataset, i.e. representing Denmark conditions, used for this study are summarized in Table S2-5. The AI not included by USEtox version 2.02 and calculated for this study, are marked in the table (†).

Table S2-5. Characterization factors (CF) estimated by USEtox 2.02, with European landscape dataset for the evaluated active ingredients in the study

CAS RN	Active Ingredient	CF USEtox 2.02			
		airC	**fr.waterC**	**agr.soilC**	**nat.soilC**
25057-89-0	Bentazon	$1.87x10^{+0}$	$2.60x10^{+2}$	$1.15x10^{+1}$	$1.15x10^{+1}$
69377-81-7	Fluroxypyr	$9.80x10^{+1}$	$4.25x10^{+3}$	$4.29x10^{+2}$	$4.29x10^{+2}$
173159-57-4	Foramsulfuron †	$1.95x10^{+1}$	$5.85x10^{+2}$	$1.61x10^{+1}$	$1.62x10^{+1}$
104206-82-8	Mesotrion †	$1.94x10^{+1}$	$1.13x10^{+3}$	$3.95x10^{+1}$	$3.95x10^{+1}$
40487-42-1	Pendimethalin	$1.77x10^{+3}$	$7.63x10^{+5}$	$2.04x10^{+3}$	$2.04x10^{+3}$
133855-98-8	Epoxiconazol	$2.17x10^{+3}$	$1.12x10^{+5}$	$2.23x10^{+3}$	$2.23x10^{+3}$
175013-18-0	Pyraclostrobin †	$1.51x10^{+3}$	$4.98x10^{+5}$	$7.31x10^{+0}$	$7.31x10^{+0}$
52315-07-8	Cypermethrin	$4.51x10^{+5}$	$1.43x10^{+8}$	$2.62x10^{+4}$	$2.62x10^{+4}$
94-74-6	MCPA	$3.95x10^{+1}$	$2.12x10^{+3}$	$8.01x10^{+1}$	$7.98x10^{+1}$
79277-27-3	Thifensulfuron-methyl	$4.49x10^{+3}$	$1.88x10^{+5}$	$4.33x10^{+3}$	$4.33x10^{+3}$
60207-90-1	Propiconazol	$2.41x10^{+2}$	$3.36x10^{+4}$	$4.18x10^{+2}$	$4.18x10^{+2}$
60-51-5	Dimethoat	$1.18x10^{+2}$	$2.01x10^{+4}$	$8.01x10^{+2}$	$8.01x10^{+2}$
94-75-7	2,4-D	$1.85x10^{+1}$	$1.12x10^{+3}$	$1.98x10^{+1}$	$1.98x10^{+1}$
1689-84-5	Bromoxynil	$3.76x10^{+2}$	$2.14x10^{+4}$	$1.39x10^{+2}$	$1.39x10^{+2}$
83164-33-4	Diflufenican	$4.63x10^{+1}$	$4.02x10^{+3}$	$3.31x10^{+1}$	$3.31x10^{+1}$
1689-83-4	Ioxynil	$4.03x10^{+2}$	$2.58x10^{+4}$	$1.02x10^{+2}$	$1.02x10^{+2}$
52888-80-9	Prosulfocarb	$1.64x10^{+2}$	$4.39x10^{+4}$	$8.96x10^{+0}$	$8.96x10^{+0}$
105512-06-9	Clodinafop-propargyl	$2.51x10^{+2}$	$6.15x10^{+4}$	$3.96x10^{+0}$	$3.96x10^{+0}$
71283-80-2	Fenoxaprop-P-ethyl	$3.23x10^{+2}$	$9.44x10^{+4}$	$4.78x10^{-1}$	$4.78x10^{+1}$
74223-64-6	Mesosulfuron-methyl	$6.94x10^{+2}$	$3.12x10^{+4}$	$6.28x10^{+2}$	$6.28x10^{+2}$
141776-32-1	Sulfosulfuron	$7.30x10^{+1}$	$7.59x10^{+3}$	$1.07x10^{+3}$	$1.07x10^{+3}$
101200-48-0	Tribenuron-methyl	$2.21x10^{+1}$	$9.92x10^{+2}$	$1.85x10^{+1}$	$1.85x10^{+1}$
999-81-5	Chlormequat-chlorid	$1.10x10^{+1}$	$2.29x10^{+2}$	$2.26x10^{+1}$	$2.26x10^{+1}$
16672-87-0	Ethephon	$6.83x10^{+1}$	$1.77x10^{+3}$	$7.54x10^{+1}$	$7.54x10^{+1}$
24307-26-4	Mepiquat-chlorid	$1.04x10^{+1}$	$2.41x10^{+3}$	$8.33x10^{-2}$	$8.33x10^{-2}$
95266-40-3	Trinexapac-ethyl	$1.61x10^{+0}$	$1.59x10^{+3}$	$3.45x10^{+1}$	$3.45x10^{+1}$
131860-33-8	Azoxystrobin	$9.75x10^{+3}$	$1.13x10^{+3}$	$1.42x10^{+4}$	$1.42x10^{+4}$
188425-85-6	Boscalid †	$1.10x10^{+1}$	$5.05x10^{+2}$	$2.26x10^{-1}$	$2.30x10^{-1}$
121552-61-2	Cyprodinil	$3.49x10^{+1}$	$3.75x10^{+4}$	$1.60x10^{+2}$	$1.67x10^{+2}$
67306-00-7	Fenopiridin †	$1.28x10^{+1}$	$6.98x10^{+4}$	$2.91x10^{+2}$	$2.91x10^{+2}$
125116-23-6	Metconazol †	$2.73x10^{+2}$	$9.25x10^{+3}$	$8.64x10^{+1}$	$8.69x10^{+1}$
178928-70-6	Prothioconazol †	$2.16x10^{+0}$	$7.83x10^{+2}$	$1.54x10^{-1}$	$1.50x10^{-1}$
107534-96-3	Tebuconazol	$1.01x10^{+3}$	$1.02x10^{+5}$	$6.16x10^{+2}$	$6.17x10^{+2}$
67375-30-8	Alpha-cypermethrin	$3.31x10^{+5}$	$1.10x10^{+8}$	$1.02x10^{+4}$	$1.02x10^{+4}$
91465-08-6	Lambda-cyhalothrin	$7.09x10^{+5}$	$3.95x10^{+8}$	$1.97x10^{+4}$	$1.97x10^{+4}$
23103-98-2	Pirimicarb	$4.02x10^{+0}$	$2.41x10^{+3}$	$3.24x10^{+1}$	$7.65x10^{+0}$
102851-06-9	Tau-fluvalinat	$5.27x10^{+3}$	$3.23x10^{+6}$	$1.51x10^{+1}$	$1.5x10^{+1}$
1918-00-9	Dicamba	$3.82x10^{+1}$	$2.45x10^{+4}$	$1.98x10^{+1}$	$1.98x10^{+1}$
82097-50-5	Triasulfuron	$1.05x10^{+3}$	$4.15x10^{+4}$	$1.44x10^{+3}$	$1.44x10^{+3}$
81777-89-1	Clomazone	$9.03x10^{+1}$	$1.02x10^{+4}$	$2.09x10^{+2}$	$2.09x10^{+2}$

CAS RN	Active Ingredient	CF USEtox 2.02			
		airC	fr.waterC	agr.soilC	nat.soilC
1702-17-6	Clopyralid	$4.05x10^{+1}$	$1.33x10^{+3}$	$3.71x10^{+1}$	$3.71x10^{+1}$
101205-02-1	Cycloxydim	$6.02x10^{-1}$	$4.12x10^{+2}$	$2.95x10^{-1}$	$2.95x10^{-1}$
2764-72-9	Diquat	$2.58x10^{+3}$	$8.68x10^{+4}$	$3.10x10^{+3}$	$3.10x10^{+3}$
1918-02-1	Picloram	$2.55x10^{+2}$	$4.66x10^{+3}$	$3.15x10^{+2}$	$3.15x10^{+2}$
111479-05-1	Propaquizafop	$2.64x10^{+3}$	$2.03x10^{+3}$	$9.94x10^{+2}$	$9.94x10^{+2}$
23950-58-5	Pronamide	$1.05x10^{+2}$	$6.30x10^{+3}$	$2.20x10^{+2}$	$2.20x10^{+2}$
173584-44-6	Indoxacarb	$1.33x10^{+3}$	$3.99x10^{+5}$	$6.46x10^{+1}$	$6.46x10^{+1}$
123312-89-0	Pymetrozine	$5.66x10^{+1}$	$1.05x10^{+3}$	$1.83x10^{+2}$	$1.34x10^{+2}$
111988-49-9	Thiacloprid †	$2.41x10^{+1}$	$9.86x10^{+02}$	$1.11x10^{+1}$	$1.12x10^{+1}$
74070-46-5	Aclonifen	$8.07x10^{+3}$	$1.00x10^{+6}$	$4.95x10^{+3}$	$4.95x10^{+3}$
1071-83-6	Glyphosphate	$5.63x10^{+0}$	$3.61x10^{+2}$	$5.08x10^{+1}$	$5.07x10^{+1}$
133-07-6	Folpet	$9.67x10^{+3}$	$1.65x10^{+6}$	$2.71x10^{+3}$	$2.71x10^{+3}$

†CF calculated in the present study

SI2-4 Pesticide use and Potential ecotoxicity impact profiles of crop production

In total 60 AI were considered and represent 98.8%, 96.7% and 99.4% of the total pesticide applications by the studied crops in 2013, 2014 and 2015 respectively.

Table S2-6. Average pesticide applications rates per crop and the total agricultural use of Glyphosate in the period 2013-2015

Crop/ Year	Application rates [kg_{AI} ha^{-1} $year^{-1}$]		
	2013	**2014**	**2015**
Maize	2.06×10^{-1}	2.00×10^{-1}	2.11×10^{-1}
Grass	3.48×10^{-2}	1.00×10^{-2}	2.00×10^{-2}
Winter wheat	$1.68 \times 10^{+0}$	5.90×10^{-1}	$1.09 \times 10^{+0}$
Spring Barley	5.80×10^{-1}	3.40×10^{-1}	3.11×10^{-1}
Rape	8.10×10^{-1}	7.62×10^{-1}	6.85×10^{-1}
Peas	$1.31 \times 10^{+0}$	7.89×10^{-1}	$1.11 \times 10^{+0}$
Glyphosate Agri-use	6.04×10^{-1}	2.65×10^{-1}	3.70×10^{-1}

Table S2-7. Total pesticide used per crop and the total agricultural use of Glyphosate in the period 2013-2015

Crop/ Year	Total AI use [Ton]		
	2013	**2014**	**2015**
Maize	39.8	38.7	39.3
Grass	9.1	3.8	3.7
Winter wheat	1241.2	495.6	936.0
Spring Barley	387.6	182.7	178.6
Rape	142.0	125.7	131.5
Peas	12.5	6.5	11.7
Glyphosate Agri-use	1333	584	804
Total	31.65	14.38	21.05

Table S2-8. Changes of active ingredient (AI) use by crop in the period 2013-2015.

CROP	AIs-IN$_{2014}$	AIs-OUT$_{2014}$	AIs-IN$_{2015}$	AIs-OUT$_{2015}$
Maize	Bromoxynil Lambda-cyhalothrin	Thifensulfuron-methyl **Cypermethrin**	Thifensulfuron-methyl	Bromoxynil Lambda-cyhalothrin
Grass		Fluroxypyr Dimethoat	=	=
Winter wheat	Folpet	Fenopiridin **Cypermethrin**	Thiophanate-methyl	Bromoxynil Ioxynil Cyprodinil Metconazole
Spring Barley	Folpet	Dicamba Triasulfuron Fenopiridin **Cypermethrin** Dimethoate		Bromoxynil Ioxynil Cyprodinil
Rapeseed	Mepiquat-chlorid	**Cypermethrin**	Thiophanate-methyl	
Peas	=	=	=	=

Table S2-9. Active ingredients with significant contribution to crop potential freshwater ecotoxicity impacts in 2013-2015. Impact scores IS_{crop_ha} in [PAF m^3 d ha^{-1}]

Crop	2013		2014		2015	
	Active Ingredient	**IS_{crop_ha}**	**Active Ingredient**	**IS_{crop_ha}**	**Active Ingredient**	**IS_{crop_ha}**
Maize	Cypermethrin	$9.58x10^{+3}$	Lambda-cyhalothrin	$6.02x10^{+1}$	Thifensulfuron-methyl	$1.22x10^{+1}$
	Pendimethalin	$2.06x10^{+1}$	Fluroxypyr	$9.27x10^{+0}$	Pyraclostrobin	$1.15x10^{+1}$
	Pyraclostrobin	$1.50x10^{+1}$	Pendimethalin	$9.01x10^{+0}$	Fluroxypyr	$1.00x10^{+1}$
Grass	Pendimethalin	$1.50x10^{+1}$	Pendimethalin	$1.04x10^{+1}$	Pendimethalin	$1.24x10^{+1}$
	Dimethoat	$1.16x10^{+0}$	MCPA	$1.96x10^{-1}$	MCPA	$2.54x10^{-1}$
	MCPA	$6.73x10^{-1}$	Thifensulfuron-methyl	$1.10x10^{-1}$	Thifensulfuron-methyl	$1.28x10^{-1}$
Winter wheat	Cypermethrin	$1.04x10^{+3}$	Lambda-cyhalothrin	$2.86x10^{+2}$	Lambda-cyhalothrin	$3.39x10^{+2}$
	Alpha-cypermethrin	$4.50x10^{+2}$	Epoxiconazol	$2.89x10^{+1}$	Prosulfocarb	$6.51x10^{+1}$
	Pendimethalin	$3.68x10^{+2}$	Pendimethalin	$2.22x10^{+1}$	Folpet	$4.64x10^{+1}$
Spring Barley	Cypermethrin	$1.26x10^{+3}$	Lambda-cyhalothrin	$3.35x10^{+2}$	Lambda-cyhalothrin	$5.54x10^{+2}$
	Alpha-cypermethrin	$5.29x10^{+2}$	Alpha-cypermethrin	$3.66x10^{+1}$	Pendimethalin	$2.35x10^{+1}$
	Lambda-cyhalothrin	$2.26x10^{+2}$	Pendimethalin	$2.56x10^{+1}$	Fluroxypyr	$9.74x10^{+0}$
Rape	Cypermethrin	$5.93x10^{+2}$	Lambda-cyhalothrin	$3.63x10^{+2}$	Lambda-cyhalothrin	$9.04x10^{+2}$
	Alpha-cypermethrin	$4.09x10^{+2}$	Pendimethalin	$2.02x10^{+2}$	Azoxystrobin	$1.94x10^{+2}$
	Lambda-cyhalothrin	$4.09x10^{+2}$	Azoxystrobin	$1.95x10^{+2}$	Pendimethalin	$1.67x10^{+2}$
Peas	Lambda-cyhalothrin	$1.36x10^{+3}$	Lambda-Cyhalothrin	$1.69x10^{+3}$	Aclonifen	$2.91x10^{+3}$
	Pendimethalin	$1.02x10^{+3}$	Pendimethalin	$1.07x10^{+3}$	Lambda-cyhalothrin	$2.64x10^{+3}$
	Alpha-cypermethrin	$8.29x10^{+2}$	Propiconazol	$6.03x10^{+1}$	Pendimethalin	$8.03x10^{+2}$

SI2-5 Sensitivity Analysis

Input parameter sensitivity analysis

As input parameter sensitivity analysis was performed on several input parameters (crop characteristics, pesticide properties, off-field emissions allocation) using Maize as an example in 2013 (Mz-13) and Peas in 2015 (Ps-15). We varied each input parameter by a factor of 2 and calculated the corresponding change in the impact score. The effect on the output due to a change in an input is measured by local sensitivity to input S_{in} [-] (Rosenbaum et al., 2018) and expressed as:

$$S_{in} = (\Delta IS_{crop\_ha}/IS_{crop\_ha})/(\Delta Input_n/Input_n) \quad \text{(S1)}$$

Where Δ IS_{crop_ha} is the resulting change of the potential, freshwater impact score (IS_{crop_ha}) over the change in input n.

Table S2-10. Sensitivity to model input parameters varied by a factor of 2 for Maize in 2013 (Mz-13) and Peas in 2015 (Ps-15)

Parameter in Mz-13	**S_{in} [-]**
Fraction of drift lost	0.95
Leaf area index (LAI)	0.02
Vapor pressure	0.001
Freshwater to soil ratio	0.93
Parameter in Peas-15	**S_{in} [-]**
Fraction of drift lost	0.76
Leaf area index (LAI)	0.07
Vapor pressure	0.0001
Freshwater to soil ratio	0.73

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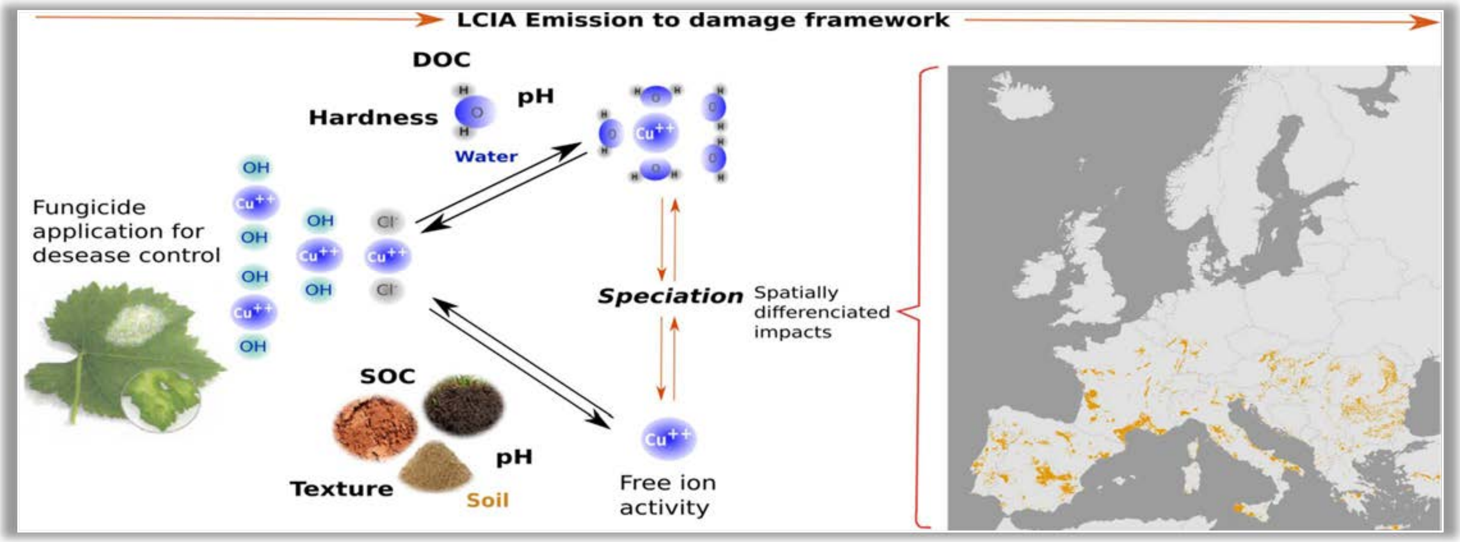

Chapter 3.

Modeling Ecotoxicity Impacts in vineyard production: Addressing Spatial Differentiation for Copper Fungicides

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Abstract

Application of pesticides is a fundamental practice for viticulture. LCA has proved to be a useful tool to assess the environmental performance of agricultural production, where including toxicity-related impacts for pesticide use is still associated with methodological limitations, especially for inorganic (i.e. metal-based) pesticides. Downy mildew is one of the most severe diseases for vineyard production. For disease control, copper-based fungicides are the most effective and used PPP in both conventional and organic viticulture. This study aims to improve the toxicity-related characterization of copper-based fungicides (Cu_Fun) in LCA studies. Potential freshwater ecotoxicity impacts of 12 active ingredients used to control downy mildew in European vineyards were quantified and compared. Soil ecotoxicity impacts were calculated for specific soil chemistries and textures. To introduce spatial differentiation for Cu_Fun in freshwater and soil ecotoxicity characterization, we used 7 European water archetypes and a set of 15034 non-calcareous vineyard soils for 4 agricultural scenarios. Cu_Fun ranked as the most impacting substance for potential freshwater ecotoxicity among the 12 studied active ingredients. With the inclusion of spatial differentiation, Cu_Fun toxicity potentials vary 3 orders of magnitude, making variation according to water archetypes potentially relevant. In the case of non-calcareous soils ecotoxicity characterization, the variability of Cu_Fun impacts in different receiving environments is about 2 orders of magnitude. Our results show that Cu_Fun potential toxicity depends mainly on its capacity to interact with the emission site, and the dynamics of this interaction (speciation). These results represent a better approximation to understand Cu_Fun potential toxicity impact profiles, assisting decision makers to better understand copper behavior concerning the receiving environment and therefore how restrictions on the use of copper-based fungicides should be considered in relation to the emission site.

Keywords Life cycle assessment (LCA) - USEtox - inorganic pesticides - freshwater ecotoxicity - soil ecotoxicity - non-calcareous vineyards

3. 1 Introduction

Although pesticides or plant protection products (PPP) are routinely applied in agriculture, one of the critical points within LCAs of agricultural systems is the lack of characterizing potential toxicity-related impacts for pesticide use in crop production. This lack is even more apparent when it comes to the evaluation of inorganic pesticides (i.e. metal-based pesticides), approved for organic farming, as these are not as well understood and characterized as synthetic[4] pesticides.

Nowadays, fungicides represent the most used active ingredients (AI) in conventional and organic agriculture, with a total annual use in the EU28 of 169,000 tons for 2014. Furthermore, Inorganic fungicides account for 39-55% of the total applied fungicides in the EU (European Commission, 2009; Eurostat, 2016).

European vineyards represent more than 50% of the total world area of vines (OIV, 2016), and the long-term use of pesticides in vineyards has contributed to increased concentrations of these substances in different environmental compartments (Hildebrandt et al., 2008; Ribolzi et al., 2002; Wightwick et al., 2008). Concerning pesticide use, one of the main differences between conventional and organic viticulture production is that in general synthetic pesticides are not allowed for use in organic pest management, whereas inorganic pesticides are indispensable for organic vine cultivation.

Furthermore, copper-based fungicides (Cu_Fun) are the most efficient and widely used PPP in Europe in both conventional and organic viticulture to control vine fungal diseases, such as downy mildew caused by *Plasmopara viticola*, one of the most severe and devastating diseases for grapevine (Agrios, 2005). Therefore, the extensive use of fungicides to control this and other fungal pests has posed significant environmental problems, such as unwanted residues in plants and water, reduction of the quality and degradation of soils, as well as some ecotoxicological threats in non-target organisms (Fantke et al., 2011a; Komarek et al., 2010). Different studies

[4] The terms synthetic pesticides and synthetic fungicides in this thesis refer to pesticides that contain xenobiotic organic compounds as active ingredients that are prohibited in organic crop and livestock production (European Comission, 2008).

have evaluated the environmental profile of viticulture and wine production from a life cycle perspective (Bartocci et al., 2017; Benedetto, 2013; Point et al., 2012). In line with LCA studies of other agricultural systems, one of the repeatedly assessed impact category for viticulture is the evaluation of global warming potential (Bosco et al., 2011; Steenwerth et al., 2015) with particular focus on water or carbon footprint indicators (Bonamente et al., 2016; Bosco et al., 2013; Lamastra et al., 2014). In contrast, impact categories related to toxicity are often disregarded, partly due to missing data for all involved chemicals including pesticides and partly due to high perceived and real uncertainties (Fantke et al., 2016; Rosenbaum et al., 2015). Consequently, pesticides and their effects on freshwater and terrestrial ecosystems are frequently omitted, even though they are one of the significant environmental concerns linked with agriculture (Meier et al., 2015). Furthermore, including ecotoxicity in LCA does not necessarily mean that the toxic effects of pesticide use are being considered. For instance, Benedetto (2013) reports pesticide emissions without including the related impact factors despite available characterization models. Other studies evaluated ecotoxicity impacts related to pesticide production but do not quantify the impacts in the use phase (Jimenez et al., 2014; Point et al., 2012). Although numerous studies acknowledge the use of copper in vineyard production, and the impacts of the production of Cu_Fun are included in a few of them (Point et al., 2012; Villanueva-Rey et al., 2014), the impact resulting from the use of these fungicides is not considered.

Freshwater ecotoxicity can be characterized with different available methods, such as the UNEP-SETAC scientific consensus model for toxicity characterization of chemical emissions in LCIA (Rosenbaum et al., 2008) that is endorsed by the UNEP-SETAC Life Cycle Initiative (Westh et al., 2015). In the case of soil ecotoxicity characterization, several emerging approaches exist (Haye et al., 2007; Lofts et al., 2013; Owsianiak et al., 2013), but no method has been yet widely adopted. Finally, there is a lack of agreement on how to assess ecotoxicity-related impacts of metal-based pesticides that are currently not adequately characterized by any existing model (Hauschild and Huijbregts, 2015; Meier et al., 2015).

Characterization of the toxic effects of metal-based emissions in LCIA assumes that the toxicity is a function of the activity of the free metal ion (Campbell, 1995; Owsianiak et al., 2015), which is related to the relevant chemical species, Cu(II). Factors such as water pH, dissolved organic carbon (DOC) and water hardness (Allen and Janssen, 2006; Gandhi et al., 2010), and soil organic carbon (SOC), soil pH and texture (Komarek et al., 2010) control metal speciation and thus its potential toxic effects. Consequently, incorporating and defining these geographically distinct characteristics in which the inventory flows (i.e. pesticide emissions) occur will have a significant influence on the ecotoxicological impact assessment of Cu_Fun AIs in LCA (Gandhi et al., 2011b; Potting and Hauschild, 2006).

The main objective of the present work is to improve the consideration of copper-based fungicides in LCA with focus on three specific aims: First, to characterize fungicide emissions and freshwater ecotoxicity impacts to compare results of copper-based fungicides with commonly used AIs to control downy mildew in European vineyards. Second, to introduce soil ecotoxicity characterization for copper-based fungicides. Third, to include spatial differentiation on the assessment of freshwater and soil ecotoxicity characterization associated with the application of copper-based fungicides in European vineyards.

We identified the most relevant aspects for modeling ecotoxicity in freshwater and soil as direct impact pathways for pesticide use. We quantified the freshwater ecotoxicity potential of the main AI (synthetic and copper-based) used to control downy mildew in European vineyards using USEtox 2.02 as characterization model (http://usetox.org). Thereafter, we estimated characterization factors (CF) for non-calcareous soils based on the multiple linear regression model developed by Owsianiak et al. (2013). Finally, we introduced geographic variability for copper-based fungicides used in European vineyards, with the truly dissolved metal fraction as proposed by Dong et al. (2014) evaluated in seven European water archetypes (Gandhi et al., 2011a) and assessed the potential soil ecotoxicity impacts in different application scenarios for specific non-calcareous vineyard soils.

3.2 Selection of active ingredients

The main fungicide AIs used to control *downy mildew*, their application practices in conventional and organic viticulture for vineyards were investigated. We selected the main AI, accepted in the EU regulation; by their effectiveness, agronomical importance and widespread use in European vineyards against downy mildew (Aybar, 2008; EFSA, 2013; MAPAMA, 2016; Renaud-Gentié et al., 2015).

The European Commission has approved the use of five different AIs of Cu_Fun (cuprous oxide, copper hydroxide, Bordeaux mixture, copper oxychloride, and tribasic copper sulfate) in both conventional and organic viticulture (European Commission, 2009). In our analysis, all copper-based fungicides will be represented by the copper cation Cu(II) as this is the prevalent species in all related fungicides (Kabata-Pendias, 2011) and the metal ion is considered the relevant part of these fungicides with respect to potential ecotoxicity impacts. As application rate for Cu(II), we used 0.918 kg ha^{-1}, which is the average value of reported application doses for treatments with copper-based fungicides in vineyards, against downy mildew, ranging from 0.18 kg ha^{-1} for tribasic copper sulfate to 2.0 kg ha^{-1} for tribasic copper sulfate. The 12 synthetic and inorganic fungicide AIs selected are presented in Table 3.1. Furthermore, all application doses used in our study were based on recommended doses for protecting vineyards against *downy mildew* for European standards and regulation (Commission, 2016; EFSA, 2013; EGTOP, 2014; MAPAMA, 2016). A complete list of the evaluated pesticide AIs, their physicochemical properties, application methods and doses and maximum residue levels are presented in the Supporting Information for chapter 3 (SI_3), Section SI_3-1.

Table 3.1 Fungicide active ingredients evaluated with their respective CAS registry numbers (RN) and recommended dose per application.

CAS RN	Active ingredient	Dose per application [kg ha^{-1}]
131860-33-8	Azoxystrobin	0.250
57966-95-7	Cymoxanil	0.121
110488-70-5	Dimethomorph	0.225
39148-24-8	Fosetil-Al	2.000
57837-19-1	Metalaxyl	0.300
70630-17-0	Metalaxyl-M	0.300
133-06-2	Captan	1.250
133-07-3	Folpet	1.500
8018-01-7	Mancozeb	1.600
12427-38-2	Maneb	1.860
9006-42-2	Metiram	1.400
15158-11-9	Cu (II) †	0.918

†The CAS numbers and specific application doses [kg ha^{-1}] for the five copper-based AIs are presented in the Supporting Information, Section SI_3-1.

3.3 Assessment framework

To quantify potential ecotoxicological impacts of the emitted fungicide fractions on exposed ecosystems, we followed the general LCIA emission-to-damage framework (Jolliet et al., 2004):

$$IS_{i,x} = \sum_i m_{i,x} \times CF_{i,x} \tag{3.1}$$

Where ecotoxicity impact scores ($IS_{i,x}$), in PAF m3 d ha^{-1}, refer to the potential impact caused by the application of an AI x to compartment i, and is expressed as the product of the characterization factor for ecotoxicity ($CF_{i,x}$), in PAF m3 d $kg^{-1}_{emitted}$, and the inventory output, that is the mass of AI x emitted to compartment i, $m_{i,x}$ [$kg_{emitted}$ ha^{-1}].

3.3.1 Emission quantification

Pesticide emissions as output of the LCI analysis ($m_{i,x}$) can be derived from applied doses and vary with application method. By obtaining information on pesticide application methods in European vineyards from experts of viticultural practices, and from statistics or literature (for more information see SI_3, Section SI3-1) we identified that the most common application method is foliar application using air blast sprayers.

Currently, only a restricted number of LCI models provide estimates of emissions to the different environmental compartments, but despite the extensive coverage regarding synthetic pesticides, climates and soils, these models are not suitable to properly assess metal-based pesticides. Based on this limitation, we assumed a static emission distribution that is dependent on the application practices to control downy mildew in vineyard production for the European context. The emission fractions were assumed to be 45% emitted to soil, 17% emitted to air and 1% emitted to freshwater, while the remaining 37% is retained by the treated crops. This assumption was based on specific percentages, or primary distributions, of fungicide application for vineyards with the air-assisted sprayer in Europe (Balsari and Marucco, 2004; Gil et al., 2014; Pergher and Gubiani, 1995; Pergher et al., 2013). This primary distribution takes into account different processes affecting the distribution of the pesticides, such as application methods and equipment, the growth stage of the vines (target retention), spray drift and drip.

3.3.2 Ecotoxicity characterization in freshwater

Characterization factors for freshwater ecotoxicity impacts of chemical emissions can be expressed as follows:

$$\mathrm{CF}_{fw} = FF_{fw} \times XF_{fw} \times EF_{fw} \tag{3.2}$$

with a fate factor (FF_{fw}), in days, representing transport, distribution and degradation in the environment; a dimensionless ecosystem exposure factor (XF_{fw}) defined as the bioavailable fraction of a chemical in freshwater, and an ecotoxicity effect factor (EF_{fw}) expressing the ecotoxicological effects in the exposed freshwater ecosystems (Hauschild and Huijbregts, 2015).

USEtox 2.02 provided CFs for freshwater ecotoxicity expressed as PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$ representing the potentially affected fraction (PAF) of ecosystem species integrated over time and exposed water volume per unit of mass of an emitted chemical $[\mathrm{PAF\ m^3\ d\ kg_{emitted}^{-1}}]$ (Henderson et al., 2011).

The freshwater impact scores (IS_{fw}) for the 12 AIs studied were calculated using eq. 3.1, where the CF for each AI was estimated using the landscape dataset for Europe in USEtox.

3.3.3 Ecotoxicity characterization in non-calcareous soils

We applied the modeling approach for terrestrial ecotoxicity characterization (Owsianiak et al., 2013) that introduces the accessibility factor (ACF) into the definition of CFs for soil ecotoxicity:

$$CF_{sl} = FF_{sl} \times ACF_{sl} \times BF_{sl} \times EF_{sl} \tag{3.3}$$

Where FF_{sl} is the fate factor representing the residential time of total metal mass in soil; ACF_{sl} is the accessibility factor defined as the reactive fraction of total metal in soil; BF_{sl} is the bioavailability factor defined as the free ion fraction of the reactive metal in soil, and EF_{sl} is the terrestrial ecotoxicity effect factor.

3.4 Spatial differentiation

3.4.1 Inclusion of spatial differentiation in the freshwater IS for Cu(II)

For the incorporation of spatial differentiation in the freshwater impact assessment $IS_{fw\text{-}EU}$, we first introduced seven European water archetypes (Gandhi et al., 2011a). These represent the variation of freshwater chemistries in Europe, and each archetype contains a specific dataset with water factors of significant influence on the speciation of Cu(II) (see SI, Section SI-2 for further details). Furthermore, three application rate scenarios (S1=0.75, S2=1.5 and S3=3 kg ha^{-1}) were derived from the most common use of copper-based fungicides in both conventional and organic viticulture, to introduce spatial aspects also in the emission quantification.

The $IS_{fw\text{-}EU}$ were calculated based on the inventory estimates and using the framework described above (eq. 3.1). The specific freshwater CFs for the EU water types ($CF_{fw\text{-}EU}$) for Cu(II) introduce in eq.2 the bioavailability factor (BF_{fw}) which is the fraction of truly dissolved metal in freshwater (Dong et al., 2014; Gandhi et al., 2010).

3.4.2 Inclusion of spatial differentiation in non-calcareous soil IS for Cu(II)

We estimated the new CF_{sl} for Cu(II) directly from soil parameters (i.e. pH, SOC, texture) for vineyards in Europe using the multiple linear regression model (MLRm) proposed by Owsianiak et al., (2013). A set of more than 20,000 European vineyards were recorded from the CORINE land cover project (EEA, 2002), and their correspondent soil parameters from the harmonized soil database HWSD (version 1.2) were selected (Fao/Iiasa/Isric/Isscas/Jrc, 2012). Geospatial analysis by means of ArcGIS (ESRI, 2017) was used to correlate the vineyards with the predominant soils of the exact areas where the vineyards were located. We only included soils with pH between 4.4 and 8.0 (typical vine growing range). Since the MLRm is not applicable to calcareous soils, soils that have a pH between 4.4 and 6.5 and carbonate content ($CaCO_3$) above 0% were excluded; also, those soils with pH > 6.5 and $CaCO_3$ higher than 10% were excluded. This resulted in 15034 non-calcareous vineyard soils for which CF_{sl} were calculated.

For estimating the IS_{sl}, we followed the modeling framework described in eq. 3.3. We estimated the impacts of 4 different application rate scenarios to simulate diverse viticultural practices across Europe. The two first emission scenarios represent standard (So1) and good agricultural practices (So2). For the other two scenarios, we tested the total maximum emission in one year of copper-based fungicide use of 6 kg ha^{-1} (So3) in organic farming (Commission, 2016) and a reduced rate of 3 kg ha^{-1} (So4) in some viticultural regions (EGTOP, 2014).

3.5 Results and discussion

3.5.1 Potential freshwater ecotoxicity impacts

Results of the freshwater ecotoxicity impact assessment for the 12 AIs aggregated over all emission compartments are shown in Figure 3.1 and impact results for the individual emission compartments are presented in Figure 3.2. There was up to 6 orders of magnitude variation in the IS_{fw} for the 12 different fungicide AIs (Figure 1), with dimethomorph (23.5 PAF m^3 d ha^{-1}) as the least potentially toxic substance and copper-based fungicides (4.6 million PAF m^3 d ha^{-1}) as the most potentially toxic AI.

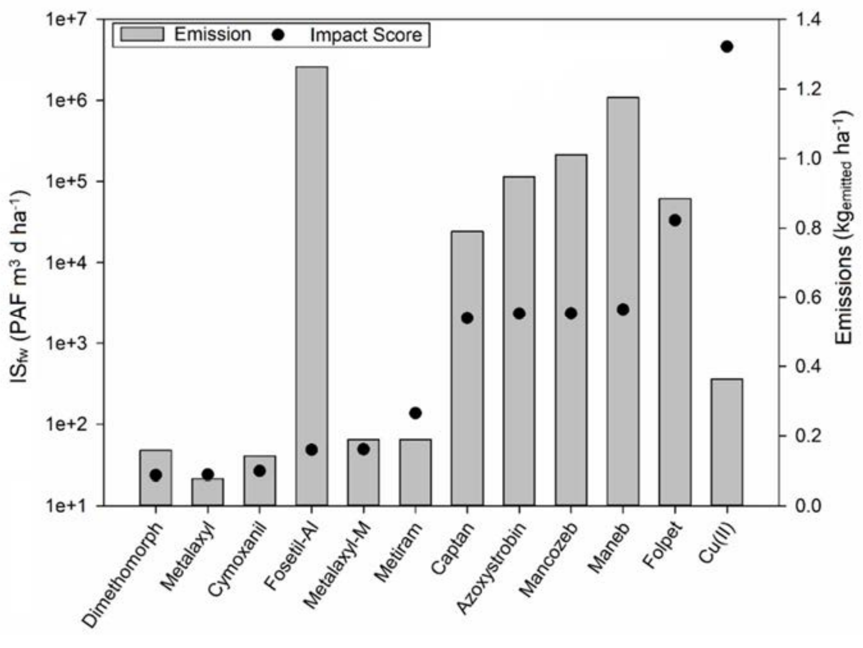

Figure 3.1. Potential freshwater ecotoxicity impact scores (IS_{fw}) [PAF m^3 d ha^{-1}] and total emissions [$kg_{emitted}$ ha^{-1}] for the 12 fungicide AIs ranked according to increasing impact scores.

In the case of the IS_{fw} for the synthetic pesticides, our findings show that fungicides, such as folpet (33300 PAF m^3 d ha^{-1}), would yield the highest potential freshwater ecotoxicity impacts if Cu(II) is not included (Figure 3.1). IS_{fw} for azoxystrobin, mancozeb, captan or maneb presented a lower potential impact despite the fact that they are emitted in similar quantities to folpet, this is mainly due to a higher EF_{fw} with respect to the other AIs (meaning also a high HC50 value). Fosetyl-aluminum is the AI with the highest application dose, but its relatively low ecotoxicity potential (48.3 PAF m^3 d ha^{-1}) ranked it as one of the less potentially impacting substances. Pesticide application doses across AIs varied ~1 order of magnitude and therefore contributed only little to the variation of the IS_{fw} across AIs over 6 orders of magnitude. These results strongly indicate that the amount of pesticide applied (pesticide use) is usually not an adequate indicator for toxicity-related freshwater ecosystem impacts in LCA, but that instead a combination of amount applied, fractions emitted, and the characterization of fate, exposure and related potential ecotoxicity effects are required.

For the few available vineyard-related LCA studies that contain potential freshwater ecotoxicity impacts, the results are not easily comparable across studies. This may be due to different methodological choices made in these studies, such as the inventory parameters considered, the methods used to estimate emissions and the impact assessment model used. Furthermore, an interesting finding of the comparison of these studies is the lack of transparency in ecotoxicity results, since many studies did not specify whether and how pesticide impacts were quantified.

Our findings regarding synthetic fungicides are consistent with results obtained by Villanueva-Rey et al., (2014), where IS_{fw} are dominated by folpet, but contrary to the results of Renaud-Gentié et al., (2015), which shows lower ecotoxicity impacts related to pesticides. The contradictory findings may be explained in the assumptions for the inventory analysis, where we have assumed fixed values of emissions for the different environmental compartments across fungicide AIs (Figure 3.2), and in consequence, our potential impact values for the synthetic fungicides differ. The authors (Renaud-Gentié et al., 2015) adapted the PestLCI 2.0 emission quantification model to be applied in vineyard production; this tool defined the technosphere as the agricultural field including the air column above it (up to 100 meters) and the soil up to 1-meter depth (Dijkman et al., 2012). This means that pesticide emissions to soil are not considered, and this could be one reason for the differences between the results in the impact assessment compared to the present study. In the case of folpet, there are further differences that are explained by the use of a CF specifically calculated in the study of Renaud-Gentié and co-authors. This highlights that following different methodological approaches can yield considerably different impact scores.

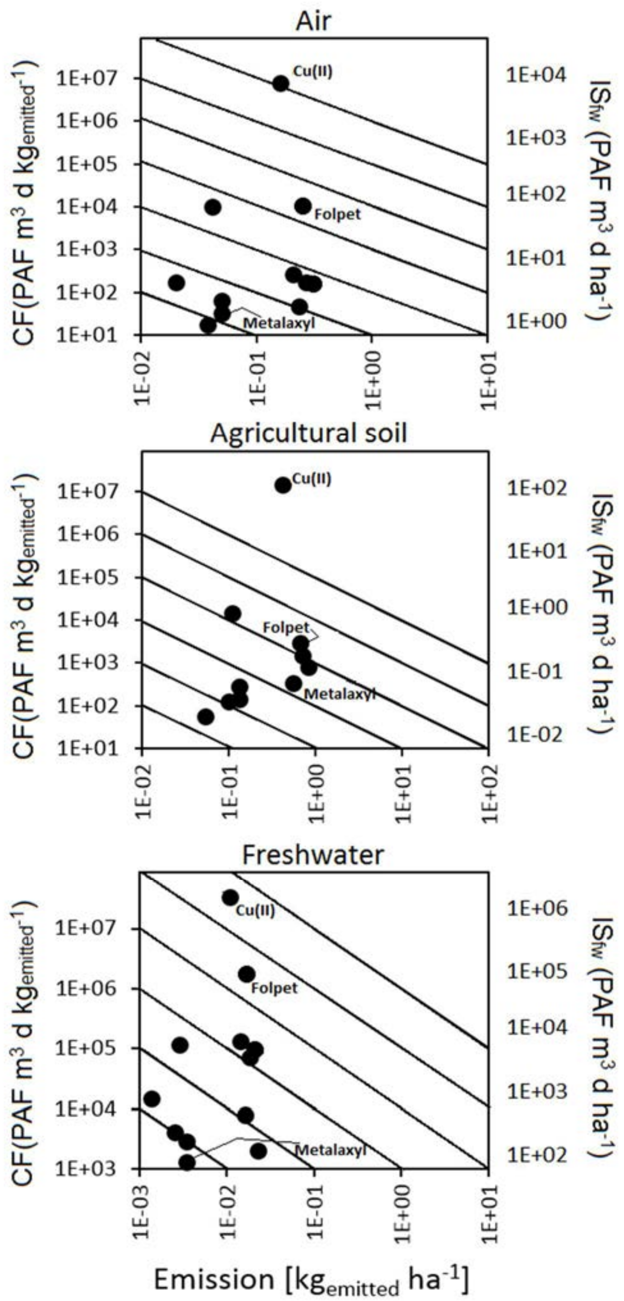

Figure 3.2 Potential freshwater ecotoxicity impact scores (IS_{fw}) [PAF m^3 d ha^{-1}] diagonalized for the 12 fungicide AIs for each of the receiving emission compartments (right-side y-axis), corresponding emissions [$kg_{emitted}$ ha^{-1}] (x-axis), and CFs [PAF m^3 d $kg_{emitted}^{-1}$] (left-side y-axis).

Although most other studies mention the use of copper in vineyards, only the work by Neto et al., (2013) and Notarnicola, (2003) include impacts for copper-based fungicides in both the production and the use phase. In Notarnicola et al. (2003), the results on impact categories are presented in aggregated percentages and not in absolute values. In that study, ecotoxicity was the most contributing impact category in the agricultural phase and depended mainly on the pesticide use. Unfortunately, there is no particular mentioning of the AI contribution to allow a comparison with our own findings. Neto et al., (2013) displayed aggregated results per impact category. They concluded that viticulture stage was the more substantial contributor to overall impact categories. Freshwater and soil ecotoxicity are due to the use of glyphosate for weed control. The results from these two studies cannot be directly compared with the results from the present study for several reasons, including the use of different inventory models, impact assessment methods and different methods to aggregate results.

Some of the challenges that constitute the main reasons why freshwater ecotoxicity assessments are not routinely included in comparative LCAs are the low availability of data and the perception of a limited reliability upon models that allow the quantification of inventories and impacts. In fact, the inclusion of potential freshwater ecotoxicity impacts provided valuable additional insight into the environmental performance of different agricultural systems in our study. The potential impacts of pesticides in organic crop production are in general lower than those reported for conventional crop production (Meier et al., 2015). However, including copper-based fungicides in the impact assessment may lead to different conclusions.

Our results emphasize that it is necessary to include copper-based fungicides with focus on the development and refinement of characterization factors, as well as, inventory emission fractions.

In the evaluation of the substance ranking, it is also important that the modeling upon which these results are based is inherently complex and subject to many assumptions and simplifications. Therefore, and since impact scores represent potential impacts rather than actual effects, our results cannot be validated against experimental data or compared with risk evaluation and must always be seen in an LCA context, where overall environmental performances of compared product systems are assessed.

Furthermore, characteristics of all AIs, such as the usage and the effectiveness for disease control, the mode of action and the metabolite formation, the increment of pest-resistant strains, among other features, should be considered when comparing different AIs for pesticide substitution treatments. Otherwise, it will be hard to identify the most viable and sustainable alternative (Fantke et al., 2015, 2011b).

Regarding the agronomical importance of copper use against downy mildew, some authors have concluded that under high pressure of the disease on organic viticulture, the only substance to offer effective control was a copper-based fungicide (Komarek et al., 2010; Spera et al., 2007). In low and medium disease pressure, alternative treatments (i.e. biocontrol agents, natural derivatives, plant extracts, etc.) may offer an adequate disease control (La Torre et al., 2011). Therefore, grapevine downy mildew control using reduced copper amounts in organic viticulture is feasible, if pest management is performed in combination with alternative treatments.

Freshwater ecotoxicity impact scores depend on several parameters, with fluctuating uncertainties. For USEtox CFs, an uncertainty range of 1-2 orders of magnitude has been determined, and the major sources of uncertainty are substances half-lives and ecotoxicity effect estimates (Henderson et al., 2011). Therefore, an AI with CF of 1000 PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$may not be (but possibly is), more toxic than an AI with CF of 100 PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$. The uncertainty of the emissions has not been quantified before and is also beyond the scope of the present study. Perhaps a more significant and probably more conclusive analysis is the inclusion of spatial differentiation for the AI that may present substantial changes due to natural variations of the emission compartment.

3.5.2 Characterization results for non-calcareous soils

Site-dependent CFs for Cu(II) in the 15034 European vineyards non-calcareous soils vary over ~1.5 orders of magnitude, with mean values equal to 2340 PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$ and spatially differentiated ranges from 155 to 7240 PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$. The results from the MLRm show that the CFs for Cu(II) are determined mainly by SOC, that influences Cu(II) mobility (i.e. metal fate) and the effects of soil pH, influencing Cu(II) bioavailability, this trend is represented in Figure 3.3. The clay content is rather poorer descriptor for the CFs of Cu(II) (2 orders of magnitude lower than SOC) and did not show a particular trend, although, is interaction with the other parameters is significant.

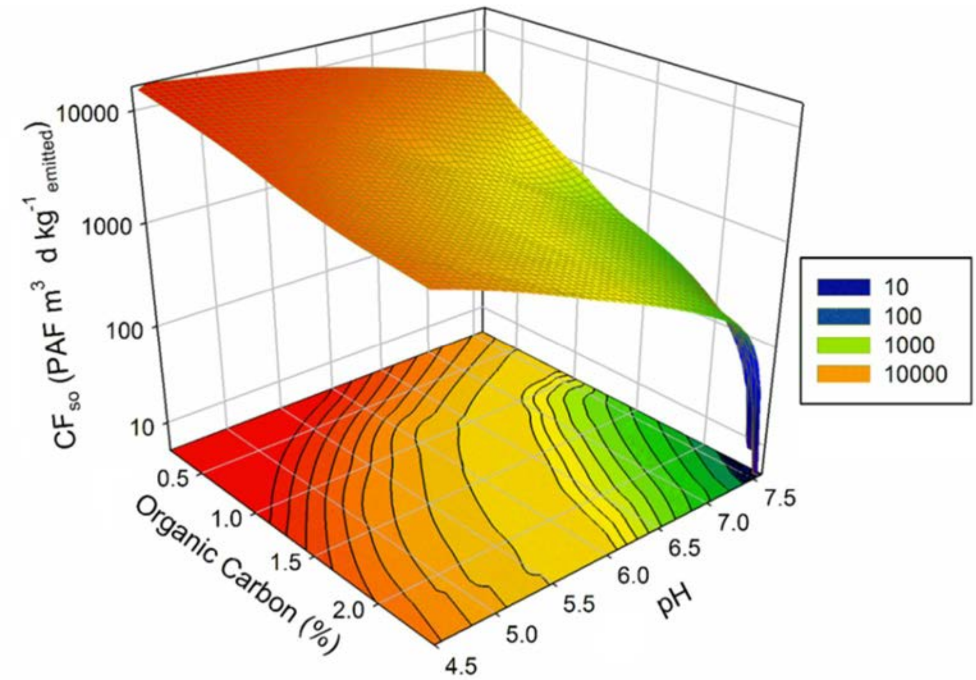

Figure 3.3 Characterization factors for 15034 non-calcareous vineyard soils CFs [PAF m^3 d $kg^{-1}_{emitted}$], calculated from soil parameters, with respect to soil organic carbon [%] and soil pH.

The parent materials of the soils (*e.g.*, clay content) influence mobility of copper in soils, clay minerals and organo-clay associations together with particular organic matter are the primary carrier phases of Cu(II) in soils. Its solubility is highly dependent on the soil pH, and it could be more available at pH values below six. In acidic vineyard soils, copper is more mobile and can more easily reach ground water. Furthermore, the mobility can be affected at pH values above ~7.5 and at this pH the formation of copper complexes (Cu-SOC) is promoted by the solubilization of SOC. Regarding copper soil ecotoxicity characterization, it is well known that the complexation of Cu(II) with SOC reduces its toxicity potential significantly. This is congruent with the trend shown in Figure 3.3. Furthermore, in a study on soils contaminated with copper it was shown that in organic soils, less than 0.2% of total copper was in the free ion form Cu(II) at pH 4.8–6.3 (Karlsson et al., 2006).

3.6 Spatially differentiated results

Our results have already shown that different factors affect the ecotoxicity of the studied fungicide AIs. In the case of copper-based fungicides, the conditions where emissions occur could be critical to determine its potential ecotoxicity-related impacts. In ecotoxicity characterization models of metals, it is assumed that the potentially ecotoxic effects on ecosystems are a function of the activity of the free metal ion. It is also well known that copper behavior (speciation and mobility) is influenced by, and substantially dependent on, the chemistry of the emission receiving environment (freshwater or soil) and thus influencing the potential ecotoxicity of Cu(II). Hence, spatial differentiation and the inclusion of site-dependent CF's are relevant when assessing impacts of copper-based fungicides (Potting and Hauschild, 2006). Such evaluation will provide a more accurate assessment of the potential impacts of Cu(II) emissions. Therefore, we present the following results for input parameters that display significant geographical variability in the quantification of IS for Cu(II).

3.6.1 Spatially differentiated freshwater impacts

Results for the freshwater ecotoxicity scenarios evaluated introducing different water chemistries are summarized in Table 3.2. The $IS_{fw\text{-}EU}$ range from 42.1 PAF m^3 d ha^{-1} (S1-EU1 water type) to 168000 PAF m^3 d ha^{-1} (S3-EU6 water type) in the seven European archetypes and across the different scenarios.

Table 3.2 ISfw-EU for Cu(II) in three different scenarios for the seven European water types.

Water type*	$IS_{fw\text{-}EU}$ [PAF m^3 d ha^{-1}]			
	Base Scenario†	**S1**	**S2**	**S3**
EU1	$1.21x10^{+2}$	$4.21x10^{+1}$	$3.16x10^{+2}$	$6.32x10^{+2}$
EU2	$5.05x10^{+2}$	$1.76x10^{+2}$	$1.32x10^{+3}$	$2.63x10^{+3}$
EU3	$1.21x10^{+3}$	$4.21x10^{+2}$	$3.16x10^{+3}$	$6.32x10^{+3}$
EU4	$2.89x10^{+2}$	$1.01x10^{+2}$	$7.55x10^{+2}$	$1.51x10^{+3}$
EU5	$1.35x10^{+4}$	$4.68x10^{+3}$	$3.51x10^{+4}$	$7.02x10^{+4}$
EU6	$3.23x10^{+4}$	$1.12x10^{+4}$	$8.42x10^{+4}$	$1.68x10^{+5}$
EU7	$1.08x10^{+4}$	$3.74x10^{+3}$	$2.81x10^{+4}$	$5.62x10^{+4}$

*Water archetypes from Gandhi et al., (2011a). †Same application dose for copper-based fungicides used for the quantification of IS_{fw}.

These results for copper-based fungicides show that water conditions with low hardness and low DOC, and medium pH, represented by water type EU6, have higher ecotoxicity potential than EU1 water type, which has a higher pH and hardness. These differences in water chemistry not only influence changes in the $IS_{fw\text{-}EU}$ but may also lead to ranking changes when comparing with the other fungicide AIs. The ~3 orders of magnitude of variation among the seven European water archetypes illustrate the relevance of the inclusion of spatial differentiation. Furthermore, if we consider the $IS_{fw\text{-}EU}$ from the base scenario, we can already see ranking changes for Cu(II) with respect to the other AIs for all European water archetypes.

It is important to stress that the variations in the $IS_{fw\text{-}EU}$ are more dependent on the different water chemistries than the dose of AIs applied. Although copper-based fungicides show higher potential impacts in freshwater ecosystems than the synthetic fungicides, variabilities in the receiving emission environment (soil or water) could make these impacts also highly variable.

On the other hand, Komarek et al., (2010) tested for a study that was conducted from 2004 to 2007 if there were substances that might replace copper in organic viticulture. One of their main findings shows that currently, there is no treatment that is as effective as copper for controlling grapevine downy mildew in organic vineyards (Komarek et al., 2010). In this context, the present study may help to understand different pest managements in various environments better, and give more accurate environmental impacts profiles. This could lead to an integrated management system in which a less efficient product is applied in combination with copper-based fungicides to reduce the total dose of Cu(II) applied, and as a consequence, reduce the overall potential ecotoxicity impacts.

3.6.2 Spatially differentiated non-calcareous soil impacts

Impact scores in non-calcareous soils for Cu(II) showed up to 2 orders of magnitude of difference in the scenarios that simulated different agricultural practices per application So1 and So2. In the same way, So3 and So4 vary 2 orders of magnitude, with values 2 times higher than So1 and So2, thereby keeping in mind that these values evaluate maximum allowed copper application in one year for copper fungicides use.

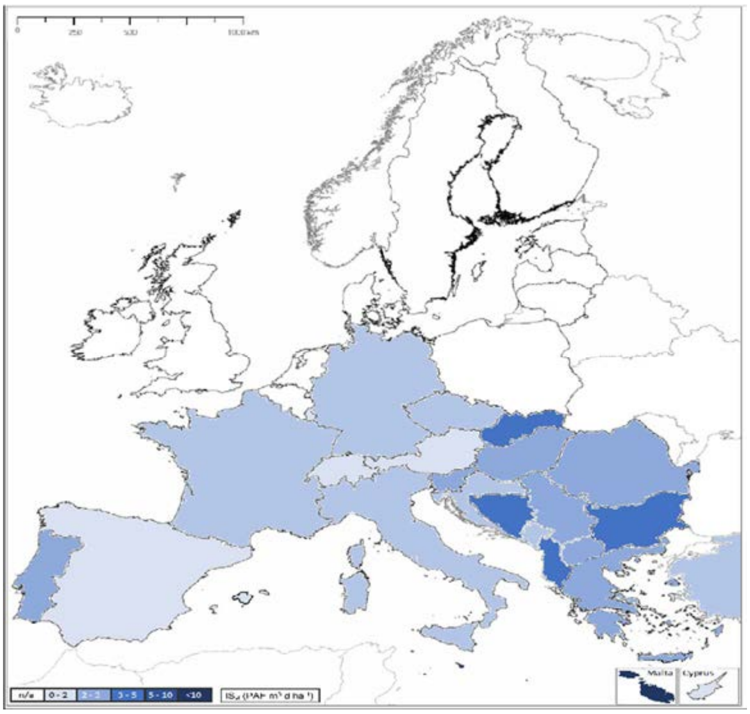

Figure 3.4 Impact scores for European vineyard non-calcareous soils (ISsl) aggregated by country for the scenario So1 that represent standard agricultural practices for copper-based fungicide application. ISsl in [PAF m3 d ha-1].

The specific soil texture and chemical composition of the evaluated vineyards varied around 2 orders of magnitude for the same application scenario. Results aggregated by country are shown in Figure 3.4 and reflect how potential IS_{sl} could vary depending on emission site. In this context, it is important to note that calcareous vineyard soils were excluded from our study; therefore, impacts occurred in this type of vineyards have not been considered. In the scenarios with more restrictive copper use, the potential impacts show a lower variation in the aggregated soil ecotoxicity impact potential per country.

3.7 Conclusions

3.7.1 Application of our results and implications for decision making

While the evaluation of global warming potentials in viticulture has been extensively analyzed in most studies, vineyard or wine-related LCAs often neglect to assess ecotoxicity-related impacts, despite their importance at a local and regional level in vineyard areas. Moreover, to the best of our knowledge, the current study constitutes an extended vision of LCIA to an agricultural product, not only through freshwater and terrestrial soil ecotoxicity evaluation but also through the inclusion of spatial differentiation and the use of emerging methodologies.

The primary outcome of our work is the potential application of these findings for LCA studies in agricultural systems. Our contribution involves assisting decision makers to understand better copper-related fungicide behavior and the importance of distinguishing its environmental impact depending on the different receiving emission environments and how restrictions on the use of copper-based fungicides should take into account the emission site.

This study has several implications for impact assessment of copper-related compounds. Considering geographic variability both in metal hazard and LCA might provide more accurate results for the evaluation of ecotoxicity impacts, and will help to draw conclusions that are more reliable in environmental impact profiles. The present study has indicated the importance of including spatial differentiation in the ecotoxicity assessment of copper-based fungicides. Accounting and evaluating for PPP potential ecotoxicity (*e.g.*, for substitution of AIs) should include variations of the receiving emission environment.

3.7.2 Limitations and future research needs

The methodology applied to characterize Cu(II) do not capture important aspects of metal speciation, such as essentiality or active plant uptake. Although the translation on the LCIA is not straightforward, because specific important spatially varying characteristics, such as cation exchange capacity describing the ionic composition of soil pore water, are not routinely measured. As demonstrated by Owsianiak et al. (2013), CFs for copper are determined mainly by OC (influencing fate) and pH (influencing bioavailability). LCIA models should, therefore, be metal-specific, and the results presented here cannot be extrapolated to other metals. In this regard, the modeling framework used in this study is only applicable to non-calcareous soils, although it is acknowledged that vineyard cultivation in calcareous soils is a typical practice in many European areas.

Further research is needed on how to account for erosion both in the emission quantification and how it might affect the impact assessment of metal-based pesticides. To our knowledge, the methods, both for impact characterization (for terrestrial soil ecotoxicity) and emission modeling of pesticides are not mature enough to be extensively applied in LCA. In this sense, this study is a first step towards to a more precise assessment of potential ecotoxicity impacts associated with agricultural production systems in general and in vineyard cultivation in particular.

If these improvements are routinely incorporated into agricultural LCAs, an important issue arises, which is, what is the most representative yet practical spatial information needed and feasible for LCAs on agricultural systems? This is a key subject that will need particular attention upon in future efforts.

Acknowledgments

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Supporting information (SI_3)

Table S3-1 Evaluated pesticide active ingredients application doses and maximum residue levels (MRL)

CAS-RN	Active ingredient	Mass g mol^{-1}	KOW -	Pvap Pa	Sol mg L^{-1}	Dose (kg ha^{-1})	MRL† (ppm)	MRL‡ (ppm)
131860-33-8	Azoxystrobin	403	$3.16x10^{+2}$	$1.10x10^{-10}$	$6.00x10^{+0}$	0.25	3	0.01*
57966-95-7	Cymoxanil	198	$1.74x10^{+4}$	$1.51x10^{-4}$	$8.90x10^{+2}$	0.121	0.03	0.01*
110488-70-5	Dimethomorph	388	$4.79x10^{+2}$	$9.84x10^{-7}$	$1.87x10^{+1}$	0.225	3	0.01*
39148-24-8	Fosetil-Al	354	$3.98x10^{-3}$	$2.72x10^{-7}$	$1.11x10^{+5}$	2.00	100	2.0*
57837-19-1	Metalaxyl	279	$4.47x10^{+1}$	$3.31x10^{-3}$	$8.40x10^{+3}$	0.30	2	0.05*
70630-17-0	Metalaxyl-M	279	$5.13x10^{+1}$	$3.31x10^{-3}$	$2.60x10^{+4}$	0.30	1	0.05*
133-06-2	Captan	301	$6.31x10^{+2}$	$1.20x10^{-5}$	$5.10x10^{0}$	1.25	0.03*	0.03*
133-07-3	Folpet	297	$7.08x10^{+2}$	$2.09x10^{-5}$	$8.00x10^{-1}$	1.50	6 - 20	0.03*
8018-01-7	Mancozeb	212	$4.17x10^{0}$	$1.00x10^{-5}$	$1.14x10^{+5}$	1.60	5	0.05*
12427-38-2	Maneb	212	$4.17x10^{0}$	$1.00x10^{-5}$	$1.14x10^{+5}$	1.86	5	0.05*
9006-42-2	Metiram	504	$2.00x10^{0}$	$1.92x10^{-11}$	$1.86x10^{+2}$	1.40	5	0.05*
Copper-based fungicides						0.918§		
8011-63-0	Bordeaux Mixture	861	$2.75x10^{0}$	$3.40x10^{-13}$	$2.20x10^{0}$	0.15-1.2	50	20
20427-59-2	Copper hydroxide	97	$2.75x10^{0}$	$1.00x10^{-6}$	$5.06x10^{-1}$	0.60-1.5	50	20
1332-40-7	Copper oxychloride	427	$2.75x10^{0}$	$1.00x10^{-6}$	$1.19x10^{0}$	0.22-1.5	50	20
1317-39-1	Cuprous oxide	143	$2.24x10^{-1}$	$1.00x10^{-13}$	$6.39x10^{-1}$	1.16-1.8	50	20
12527-76-3	Tribasic copper sulfate	461	$2.75x10^{0}$	$3.40x10^{-13}$	$3.42x10^{0}$	0.76-2.0	50	20

† Values for table and wine grapes
‡ Values for grape leaves
* Indicates lower limit of analytical determination
§mean value for application dose

Table S3-2 7 European water archetypes representing the variation of freshwater chemistries in Europe and specific water factors

Freshwater archetype	pH	DOC (mg l^{-1})	Hardness (mg $CaCO_3$ l^{-1})	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Na^{+} (mg l^{-1})	K^{+} (mg l^{-1})	SO_4^{2-} (mg l^{-1})
EU Archetype 1	8.1	8.4	221	56.6	19.5	65.8	0.1	67
EU Archetype 2	7.6	6.1	132	42.48	6.22	26.67	3.52	48.03
EU Archetype 3	8.2	1.7	169	58.51	5.59	2.6	0.78	9.61
EU Archetype 4	7.3	17.8	165	52.1	8.58	11.79	0.82	109
EU Archetype 5	6.7	2.2	78	20.3	6.7	17	0.1	67
EU Archetype 6	6.4	1.6	28	6.69	2.65	7.2	2.82	85.5
EU Archetype 7	5.9	8.9	10	2.48	0.95	6.39	1.8	2.88

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Chapter 4.

Towards a consensus to estimate global emission fractions of pesticides: Definition of application scenarios

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Manuscript under preparation.

Abstract

For agricultural pesticides, typically only the mass applied to the field is known, while there is currently no agreement on how to quantify related environmental emissions for all pesticide-crop combinations at the global scale. This is a practical challenge in life cycle assessment (LCA) for comparing pesticide application in different agricultural practices and regions. In response to this challenge, an international effort was initiated to reach agreement on recommended default agricultural pesticide emission fractions for use in LCA. In the frame of this global effort, the current study focuses on the establishment of default scenarios for agricultural practices. Aiming to define a specific set of pesticides, crops and application methods scenario combination for estimate global emission fractions of pesticides applicable for life cycle assessment, and present the consensual recommendations for this task of the pesticide effort. As a baseline, the influencing factors affecting pesticide distribution and emissions were defined. Afterwards, all inputs required to run the scenarios were collect and classified. Second, the preset scenarios were constructed and the core components further related. Experts were consulted in different stages of the study until the final scenarios were agreed, meaning that this working process was iterative. The application scenarios defined capture the critical factors for determining pesticide distribution in a representative variety of cropping systems. The main strength of these developed scenarios is the transparency and open development in every step of the process, comprising the acceptance of different stakeholders and the scientific support of experts involved in the consensus effort.

Keywords Life cycle assessment (LCA) - Agriculture – Environmental impacts – Emission quantification – Cropping systems

4.1 Introduction

Pesticides are intended to serve as plant protection products (PPP), helping to prevent, undermine, kill, or otherwise dismays pests and diseases. Although pesticides have beneficial outcomes, they also have drawbacks and potential environmental problems (Carlson, 1962). Furthermore, population growth, land competition, and the pressure to enhancement yield productions are leading towards a more intensive use of pesticides. Hence, agricultural pollution by the use of pesticides is a cause of significant concern for the general population. This nuisance is reflected in more public and political attention on the sustainable use of pesticides, as well as in a reduction of their diffuse pollution.

To meet local (national action plans - NAP), regional (EC, 2009), and globally sustainable development goals (United Nations, 2015), agriculture and food production systems need to be improved to move towards more sustainable farming practices, and therefore, to more sustainable use of pesticides. Recent studies have suggested a research agenda for agricultural sustainability that is further supported by national and international strategies (Sala et al., 2017; Soussana, 2014). In this perspective, integrated pesticide management (IPM), low input and organic agriculture have been promoted as more sustainable alternatives to conventional agriculture (Bucur, 2013; OECD, 2000; Rossi et al., 2012).

Holistic approaches such as life cycle assessment (LCA) are frequently accepted in the effort to account for the environmental performance of different production systems. Also, LCA models are supported by cause-effect relationships in different environmental compartments, which allow understanding the environmental consequences of human interventions. However, a practical challenge for LCA of agricultural systems is the comparison between different farming practices. This is especially true when considering pesticides use, which is further affected by significant inconsistencies within the inventory and the impact assessment phase (Meier et al., 2015; Notarnicola et al., 2017; Rosenbaum et al., 2015).

Commonly, the understanding of agricultural practices through LCA approaches results intricate when the quantification of the proportion of pesticide active ingredient (AI) emitted to the different environmental compartments is based only on the dose applied to the agricultural field. There are very different approaches and assumptions that are currently applied in quantifying LCI of pesticides (e.g., Ecoinvent (Nemecek and Kagi, 2007), the US field crop

LCI database (NREL, 2016) or the organic pesticide emission model PestLCI (Birkved and Hauschild, 2006; Dijkman et al., 2012). In general, these approaches offer inconsistent results which are partially overlapping (spatially or temporally) the impact pathways for pesticide use. Besides, these tend to be not compatible or comparable, and therefore, they influence the impact assessment results. As a consequence, these approaches may not represent realistic conditions in LCA studies involving agricultural systems (Peña et al., 2018; Rosenbaum et al., 2015).

On the other hand, it is well established that processes and conditions such as deposition, volatilization, leaching, runoff, and plant uptake, predominantly influence fate and behavior of pesticides. Moreover, all these processes depend on many factors, for example, the physicochemical properties of the AI, the application method and machinery, crop physiognomies, the weather conditions and soil characteristics (Fantke et al., 2011; Renaud-Gentié et al., 2015; van Zelm et al., 2013). All this processes and factors generate complexity, making the preparation of inventories particularly difficult and denote a significant obstacle to understand the distribution and transport of a pesticide after its application to the agricultural fields, and to quantify emissions to environmental media. Therefore, understanding and simplifying these processes and factors are essential to a realistic evaluation of pesticides impacts (Reichenberger et al., 2007; Zhang et al., 2018).

Environmental fate of a chemical emission in LCA is typically modeled during the impact assessment (LCIA). However, given the significant influence of the local conditions to transport processes from the pesticide application to environmental compartments (i.e. air water, agricultural soil and natural soil), the first moments of environmental fate of pesticides should be considered as part of the inventory modeling (Rosenbaum et al., 2015; van Zelm et al., 2014).

As a response to the needs for harmonization of the current modeling approaches including the assumptions for system boundaries, the interface between inventory and impact assessment, and the definition of default scenarios for specific practice and systems, a global effort started in 2012 under the Tox-Train project funded by the European Commission (DTU, 2016). This effort aims to arrive at a consensus on how to quantify pesticide emission fractions for use in LCA.

In the frame of this global effort, the current study focuses on the establishment of default scenarios for agricultural practices. Aiming to define a specific set of pesticides, crops and application methods scenario combination for estimate global emission fractions of pesticides applicable for life cycle assessment, and present the consensual recommendations for this task of the pesticide effort.

4.2 Methodology to define application scenarios

4.2.1 The pesticide consensus effort: brief history and framework

With the goal of defining, developing and agreeing on the quantification framework, inputs and outputs towards a set of pesticide emission fractions for use in LCA, a global effort was originated in 2012 (Fantke et al., 2017). In this context, different workshops along with distributed tasks for research teams in between the workshops were organized (see, Figure 4.1) involving more than 100 specialists representing different stakeholders from the five continents (Fantke et al., 2017).

The scoping workshop held in Glasgow (UK) in 2013, provides guidance on the delimitation between LCI-LCIA and further recommends on how to consistently account for emissions and impact assessment concerning pesticide use in agriculture (Rosenbaum et al., 2015). Furthermore, different tasks to evaluate state of the art on emission modeling and address current challenges for the emission quantification were conducted as a follow-up for this workshop. In a further step the framework workshop (Basel, Switzerland in 2014), defines a set of data and models that can be consistently combined and used it as a common emission quantification framework. Moreover, based on the findings of this workshop several tasks were identified and carried out as part of the work to calculate default values for emission fractions depending on the conditions of the pesticide application (Fantke, 2016a). One of those tasks was the development of archetypical and aggregated set of scenarios across crops and agricultural practices for simplification, and therefore, the starting point for the present work (Figure 4.1).

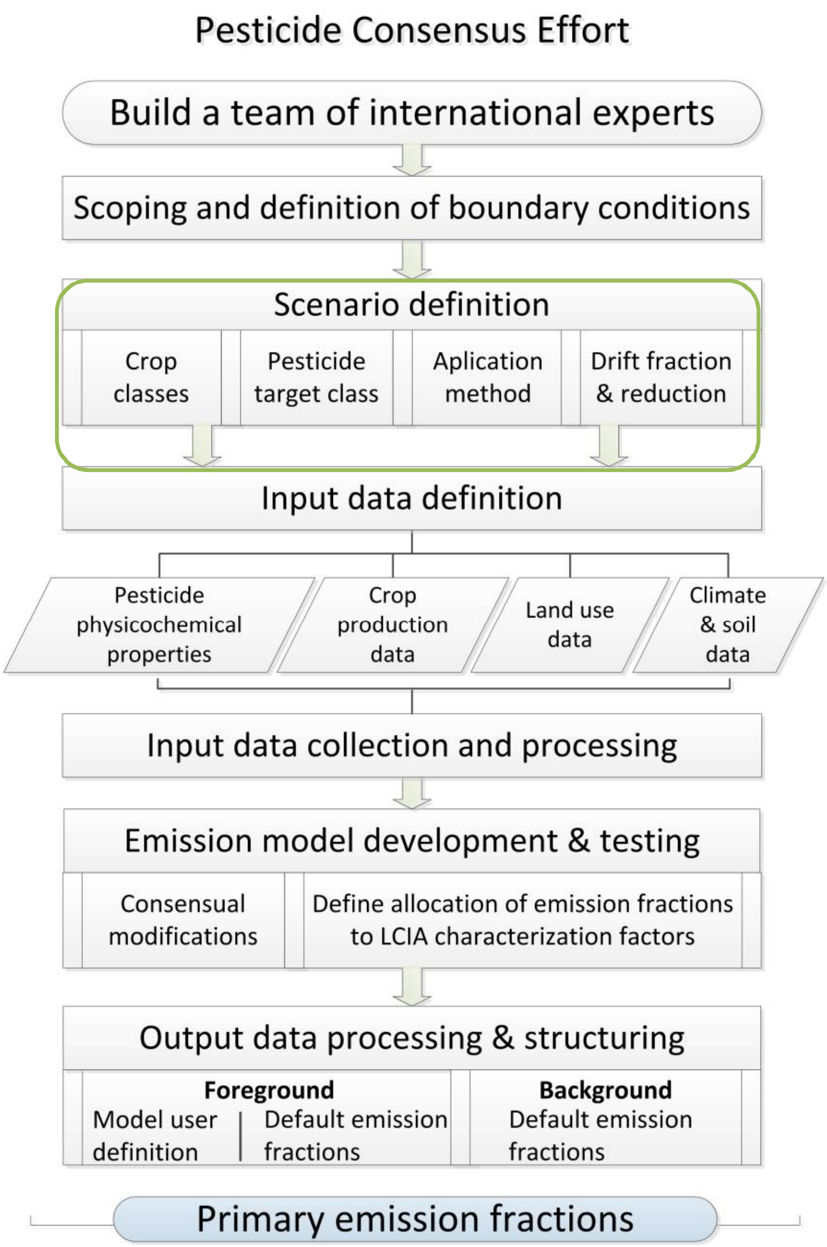

Figure 4.1 Overview of the identified and distributed working steps towards the pesticide emission fractions for use in LCA, in the frame of the pesticide consensus effort. In green highlighted, the task advanced within this study.

At a further step a preset of representative archetypes, for pesticides, crops and application methods were pre-defined (the steps followed to this end are further explained in section 4.2.2). This advanced scenarios and the modifications on the calculation framework toward a consensual emission model, developed by other teams involved in the effort, were presented and discussed at the consensus workshop (Bordeaux, France in 2015). In this building workshop, a consensual agreement was reached on the modeling framework, the output format for the emission results, the data associated for the implementation and the default scenarios to be recommended for LCA (Fantke, 2016b). The scenarios were further refined (as described in section 4.3) and used as input for the first test of primary emission fractions per country and by pesticide target class (the later been carried out by other team involved in the modeling task) (Grant, 2016), and presented together in the stakeholder workshop held in 2016 in Dublin (Ireland) (Fantke, 2017).

4.2.2 Steps towards scenario definition

As a baseline, the influencing factors affecting pesticide distribution and emissions were defined. Once applied, pesticides move off the treated crop into the environmental media. This movement (to specific target zones on the plant) can be beneficial, but also can transform pesticides as potential pollutants affecting air, water resources, wildlife, beneficial insects, and other crops. The process with significant influence on pesticide distribution and transport, and hence on the emissions fractions to environmental media are presented in Figure 4.2.

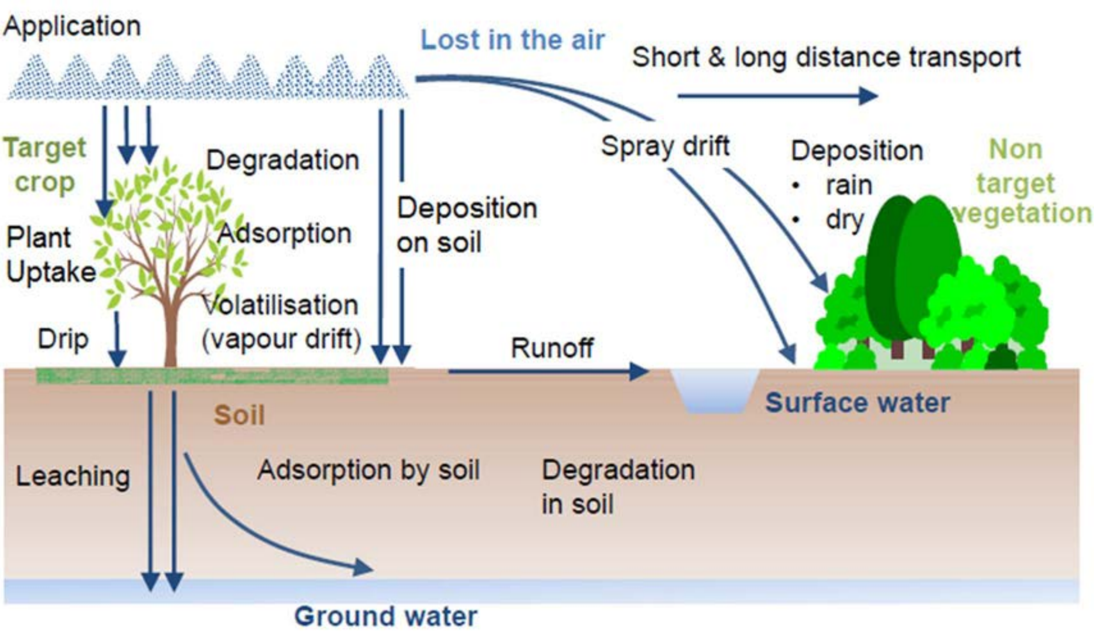

Figure 4.2 Pesticide distribution and pathways of transport. Adapted from Rossi (2012).

Different pesticide fractions may be directly emitted to air, soil, and, in some cases, to surface water (Figure 4.2). Drift and runoff have been recognized as two of the most relevant process for distribution and transport (Holterman et al., 2017; Reichenberger et al., 2007). Many studies also include deposition, volatilization and plant uptake (Cryer et al., 2001; Davie-Martin et al., 2013; Fantke et al., 2011; Lebeau et al., 2011). At the same time these processes are govern and influenced by different factors, such as the pesticide product (hence, the AI), the application method and equipment, the conditions (i.e. weather) in the area, the crop class (canopy morphology) and the existence or not of buffer zones (Fantke and Juraske, 2013; Renouf et al., 2018; Rosenbaum et al., 2015). In the present study, these influencing factors are assessed for the establishment of default application scenarios. Furthermore, the recommendations about the data requirements to perform a representative LCI for pesticide use were followed (Fantke, 2016a; Rosenbaum et al., 2015).

The overall information flow for defining and developing an archetypical and aggregated set of scenarios across globally occurring agricultural practices builds on several steps, presented in Figure 4.3.

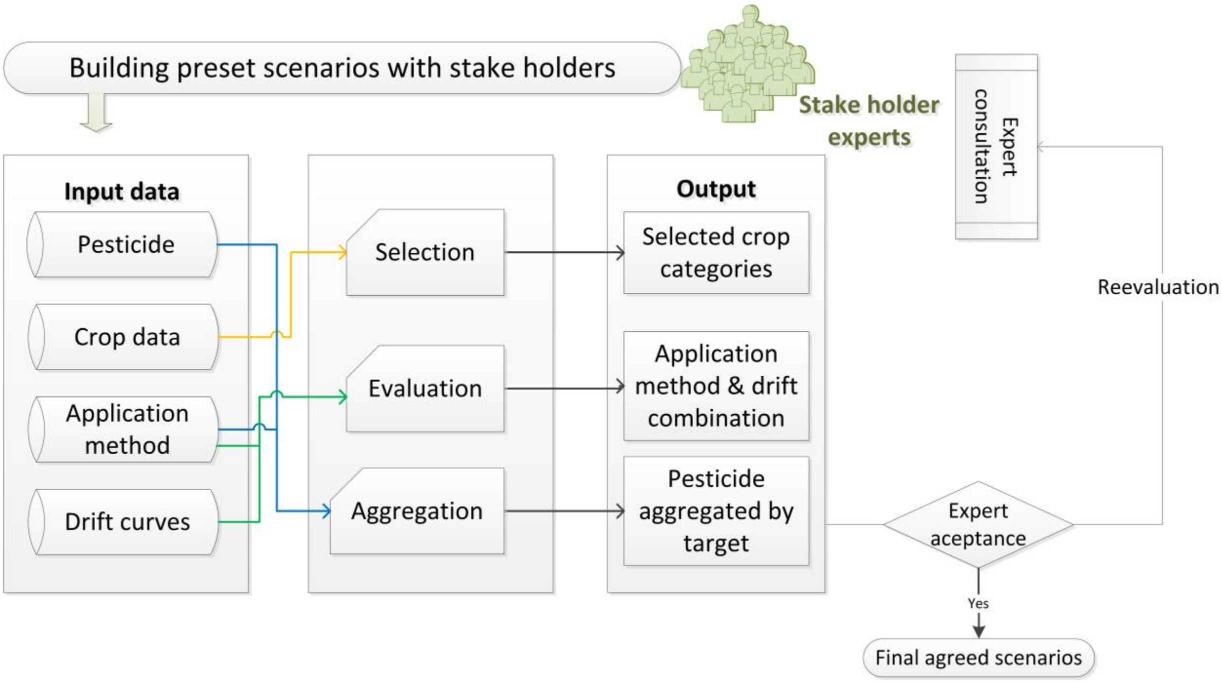

Figure 4.3 Diagram of the followed steps for defining and agreeing on application scenarios.

The first step, once the factors affecting pesticides emission were identified, was to collect and classified input required. Second, the preset scenarios were constructed and the core components further related. Experts were consulted in different stages of the study until the final scenarios were agreed, meaning that this working process was iterative.

4. 3 Results

4.3.1 Crop class selection

Selecting crop classes is essential for estimating default global emission fractions of pesticides. The crop classification reflects several elements related to crops, including the crop species, the variety, the morphology and the growing cycle. To define the crop class for the application scenarios more than 172 different types of crops were identified. In this sense, and to facilitate data collection, statistical tasks and future comparisons, the FAO classification was selected as a starting point (FAO, 2010). To delimitated crop classes, the morphology of the crop was a central point, given its close relation to define pesticides application method and equipment. Likewise, the global agricultural production data (FAOStat) was the base for the selection of the different crop classes to be used in the study.

It is difficult to find the right balance on how much simplification can be feasible, without losing reliability on the definition of scenarios. Thus, the further inclusion and refinement of the crop classes were made accounting as much as possible for different agricultural and crop characteristics, but without forgetting, the simplification needed for modeling proposes. Crop classes, then, were further aggregated and allocated following, additionally to FAO classification, the central product classification (CPC) (UN, 2015) and expert advice. Finally, crops were classified into 18 crop classes and several example crops within each class (Table 4.1).

Table 4.1 Defined crop classes, crop examples within each class and the central product classification (CPC).

Defined crop class	Crop examples
Berries	Strawberry, cape gooseberry, **CPC** 135, 135-
Citrus fruits +Olive	Orange, lemon, lime, grapefruit, olive **CPC** 145, 132, 132-
Fruits temperate	Apple, pear, apricot, peach, nectarine **CPC** 13, 134, 134-, 1239,1315
Grapes/Vines	Grape **CPC** 133, 1351
Malvaceae	Cotton **CPC** 192-

Defined crop class	Crop examples
Nuts	Almond, chestnut, hazelnut, pistachio **CPC** 137, 137-
Oil-Bearing crops	Sunflower, rapeseed, soy bean, peanut **CPC** 14, 14-, 144-, 1319,
Oil-Bearing trees +Banana	Palm oil, coconut, banana, plantain, **CPC** 146, 1491, 1313, 1312
Other permanent crops	Coffee, cocoa, tea **CPC** 16, 16-, 19-, 165-, 1691
Paddy rice	Paddy rice **CPC** 113
Panicoideae	Maize, sorghum **CPC** 112, 114, 1911, 1214
Poaceae	Sugar cane **CPC** 18, 1802
Pooideae	Wheat, barley, oat, rye, barley, quinoa **CPC** (cereals) (Forage) 11-, 119-, 1199
Pulses	Beans, lentils, peas, vetch, lupin, cheakpea, cowpea **CPC** 124, 170-
Roots and tubers	Potato, yam, cassava, taro, onion, garlic **CPC** 15-, 125-, 125, 127, 194
Tropical and subtropical fruits	Sub-tropical/tropical fruits (mango, guayaba, papaya, date) **CPC** 131, 131-
Vegetables fruit	Fruit solanacees, cucurbitacees (passionfruit, lulo, maracuya) **CPC** 122, 122-, 123-, 124-
Vegetables leafy	Cabbage, lettuce, cauliflower, broccoli **CPC** 12, 121-, 129, 1243, 1919

Once the crop class aggregation was performed, we need to intersect the crop classes with spatial data to generate the full set of scenarios. This contribution of each crop class to the overall land area is relevant to calculate the default values for pesticide emissions at a global scale. To this end, an extrapolation from crop specific harvested area and crop class were made. Data from FAOstat (FAO, 2016) and EARTHStat (UBC, 2016) by crop item harvested area was used (average over last 10 years for all values), to aggregate over crops to match the selected crop classes; obtaining a global value for harvested area (ha) by each one of the 18 crop class. One example of this classification is presented in Figure 4.4.

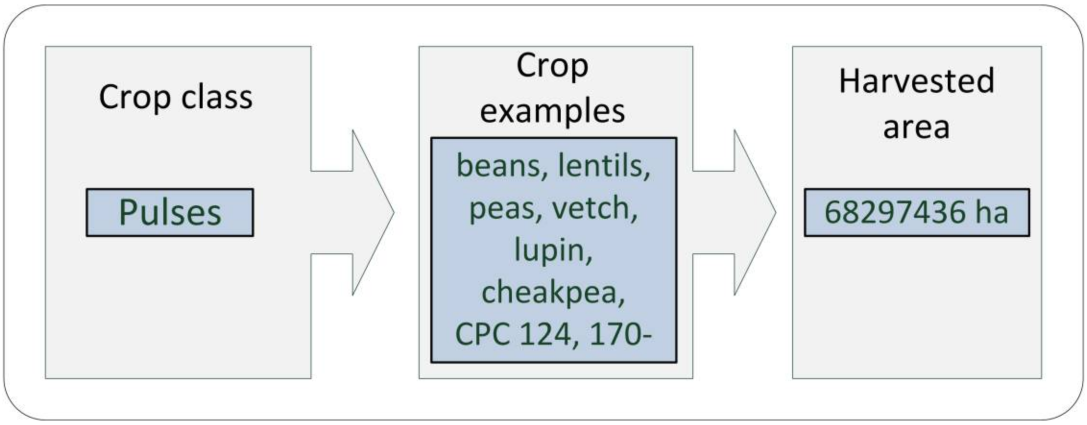

Figure 4.4 Example for pulses of the selected crop classes with the corresponding harvested area (ha).

4.3.2 Pesticide classes and aggregation

Pesticide or plant protection products (PPP) are standard terms that include several classes of substances. These substances differ in their physical and chemical characteristics from one to another, but also, can be classified based on shared properties. Nowadays, there are many methods of pesticide classification (e.g., based on the mode of action, the sources on origin, the spectrum of action, the formulation, the toxicity level, among others). Three of the most popular classes comprises: i) the classification based on the chemical composition of the AI, ii) the classification based on the mode of entry, and iii) the classification based on the pesticide function and the organisms they kill (Yadav and Devi, 2017).

The most used classification is the one based on the chemical composition and the nature of AI. This classification provides a clue on the physical and chemical properties of the pesticides. However, the chemical based classification is rather complex, because in general modern pesticides include both plant origin and synthetic AI, from which organic and inorganic AI can be further divided into many categories. For example, synthetic-organic-insecticides can be further classified as organophosphates, carbamates or pyrethroids, to mention some.

The ways pesticides come in contact or enter the target are known as modes of entry. Based on those modes of entry, pesticides can be classified as stomach poisons (ingestion), systemic, contact, fumigants and repellents. Even though this classification reduces complexity; the AI cannot be further related with the crop class - application method combination, hence do not allow us to define proper application scenarios.

Finally, under the classification method based on the pesticide function, AI are categorized based on the target pest(s) or organism(s) they are intended to kill or affect (e.g., larvicides, ovicides, nematicides, among many others), or the function they have over those targets (e.g., chemosterilants, defoliants, desiccants, etc.). In addition, some AIs can have multiple but equal effects to control different pests and may be considered in more than one pesticide class (e.g., metam sodium/potassium can be equally classified as fungicide, insecticide and nematicide). Given the versatility and the potential for further aggregation, this classification method was chosen.

Following the EU – Pesticides Database (EC, 2016) and the guidance for selecting input parameters in modeling fate and transport of pesticides (US-EPA, 2009), more than 30 different target classes were identified. From those, 13 key target classes were determined and finally aggregated into nine definitive pesticide classes (see, Table 4.2). This aggregation was made considering that in practice many pesticides are applied to the same application method; furthermore, depending on the crop class the same equipment may be used to apply different pesticides.

Table 4.2 Defined pesticide target class.

Defined Target Class	Examples
Acaricide / Miticide	Abamectin, Malathion
Attractant / Repellent	Dodecyl acetate
Fungicide	Pyraclostrobin
Insecticide	Thiacloprid
Herbicide	Bentazone
Molluscicide	Ferric phosphate
Nematicide	Oxamyl
Plant growth regulator	Ethephon
Rodenticide	Magnesium phosphide

Finally, this aggregation was also made taking in account the pesticide list, which another task group was collecting, allocating all AI into one of the defined target class. Moreover, different practices accounted in the aggregation process follow the scientific opinion of different experts involved in the consensus effort.

4.3.3 Application methods and drift association

Along with crop characteristics and pesticide active ingredients, application methods affects pesticide emission fractions, since diverse equipment and practices show different potentials for drift and many other distribution processes (van de Zande et al., 2007). Nowadays there are many types of equipment and machinery for pesticide application in agricultural production. A review of the most used equipment in different agricultural systems was performed. At a first step, the pesticide application methods and areas of use were divided into seven categories and eight subcategories. Second, the spray application equipment was dived by orientation (i.e. vertical or horizontal), volume and sped. Third, a first aggregation was completed to create nine application method categories, summarized in Table 4.3.

Table 4.3 Summary and description of application methods categories.

Application Methods	Description	Image
Hand operated sprayers	This category includes trigger pump sprayer, gun sprayer, backpack sprayer, knapsack sprayer, among others. These sprayers can vary widely in type and pressure capability. However, their distinguishing feature is the extension that ends in an adjustable nozzle, with a hose attached to a small portable tank or larger stationary container.	
Boom Sprayers	Boom sprayers have multiple nozzles spaced over the length of the boom. Tractor mounted booms sprayers are generally used to broadcast liquid pesticides over large areas. The nozzles are directed towards the ground, and boom widths ranging from 6 to 36 meters.	
Air-blast sprayer	Air-blast sprayers are most often used on orchard crops, grapes and some berry crops. Have nozzles placed in a very high-speed air stream produced by a fan. The air stream propels the very fine spray droplets to the target. Also, the air stream creates leaf movement, allowing better coverage of insecticides and fungicides.	
Aerial applicators	Aircraft and helicopters are used for applying pesticides either as a solid or liquid, including ULV spray. Aircraft are mostly used for large, continuous areas that may be sprayed with a minimum number of turns. Helicopters are useful for treating discrete or isolated patches.	

Application Methods	Description	Image
Granular applicators	Are available to broadcast pesticide granules over an entire field surface or in bands that correspond to crop rows. Application equipment may use gravity or a positive metering mechanism to regulate the flow of granules. Small, hand-operated granule dispersal equipment (e.g., push rotary spreaders) may be used to treat smaller areas such as in landscaping.	
Fumigation, foggers, Low Volume (LV), Ultra Low Volume (ULV) Sprayers	Thermal foggers: use heat to vaporize the pesticide into a highly visible dense fog. LV and ULV sprayers: also known as "cold foggers", use concentrated pesticides with no carrier. Cold fogging produces small droplets using individual nozzles to break up the liquid droplets. As the droplets are microscopic, the spray area is increased.	
	LV or ULV Sprayers are used by small farmers in Africa mainly on cotton crops. A spinning disk moved by an electric motor spreads the product in very small droplets.	
Chemigation	Chemigation is the application of pesticides to crops through the irrigation system by mixing the AIs with the irrigation water.	

This set of application methods was a combined with a review of databases and expert, technicians and agronomist opinions, regarding the most common application method per crop class-target class combination. This refinement was done having in mind the most representative agricultural practices for different regions, including tropical ones, and the availability of drift models that help to describe this specific process. On the other hand, as the application method is one of the primary factors determining drift a further step was performed to define suitable air emission and drift reduction fractions per all application and crop class combination.

For example for field crops, pesticides are most commonly applied using boom sprayers, in this case, pesticides are usually diluted in water and distributed in the field by atomizing the liquid into droplets from nozzles. For such a case (e.g., field crop and boom sprayer), various spray drift functions and models have been developed (Butler-Ellis and Miller, 2010; Holterman and van de Zande, 2003; Lebeau et al., 2011). In orchards, different types of sprayers are used (e.g., for fruit crops, trees, tall crops, so on) but still some underlying principles are comparable. For example, the droplets are distributed more or less horizontally or even upward into the crop using air flow. In this cases spray drift are significantly higher than those for field crops and drift functions have also been previously developed (Ganzelmeier and Rautmann, 2000; Holterman et al., 2017).

The selected application method and associated drift functions were assigned to the corresponding crop and pesticide target combinations. To further differentiate application practices, when possible drift reduction was also integrated into the scenarios by the use of anti-drift nozzles, shielded or air assistance equipment (e.g., fungicide application to grape vines and anti-drift nozzles) obtaining the final application scenarios.

4.3.4 Resulting application scenarios

In total 84 different default scenarios for agricultural practices were defined for a specific set of pesticides, crop classes, and application methods associated to wind drift fractions and drift reduction types. These scenarios were used to cover the principal globally occurring pesticide application practices. Furthermore, these scenarios were coupled with psychochemical data for pesticides and with global data for climate, soils and land use; and used as an input for estimate global emission fractions of pesticides applicable for life cycle assessment, in the context of the pesticide consensus effort.

To illustrate the applicability of the application scenarios, two practical examples were carried out. The first is a follow-up to the case illustrated in section 4.3.1 through all the steps for the archetypical classification. The second compares realistic agricultural data and the output using the application scenarios.

Example 1: Archetypical classification for the case of pesticide treatments for pulses

The Resulting archetypical classification for insecticide application on lentils is illustrated in Figure 4.5. This shows the result of following all the steps until the definition of a specific application scenario for the selected example.

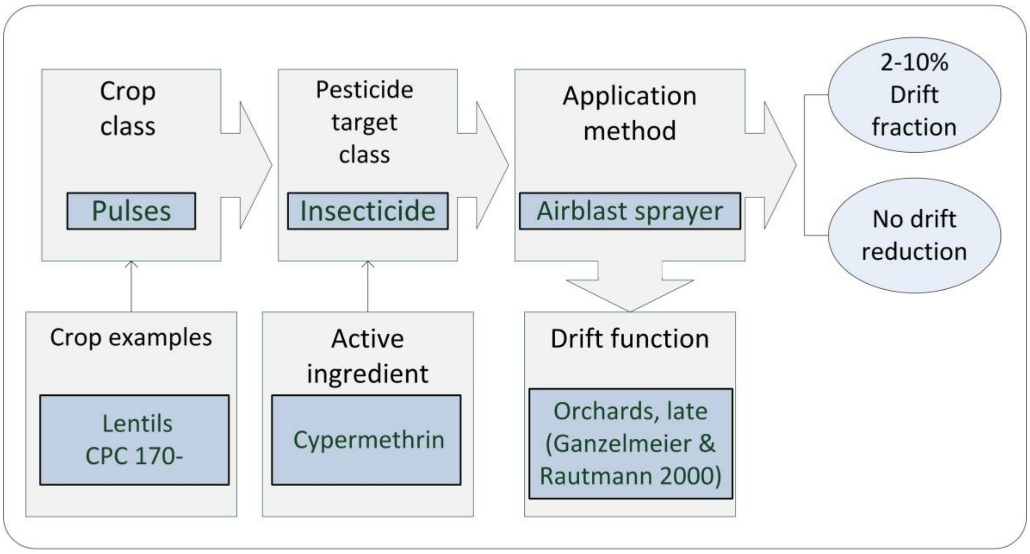

Figure 4.5 Illustration of scenario definition for insecticide application on lentils, a practical example.

Example 2: Realistic application data and application

To compare the output results of the different scenarios defined, the application practices for treating specific diseases in 13 different crops were investigated. The agricultural data and the archetypical classification of scenarios combining crop class, pesticide target class and application method, for the selected pesticide treatments are presented in Table 4.4.

Table 4.4 Results for the illustrative example of realistic application practices and the application scenarios defined in the study.

Realistic application practices				**Results for application scenarios**		
Crop	**Pest or disease**	**Active ingredient**	**Dose kg_{AI} ha^{-1}**	**Crop class**	**Pesticide target**	**Application method**
Banana	Banana weevil	Azadirachtin	0,038	Oil-Bearing trees + Banana	Insecticide	Air-blast sprayer
Barley	Weeds	Pendimethalin	1,65	Pooideae	Herbicide	Boom sprayers
Corn	Weeds	Mesotione	0,12	Panicoideae	Herbicide	Boom sprayers
Grape	Mildew	Fosetil-Al	0,16	Grapes/ vines	Fungicide	Air-blast sprayer
Green peas	Weeds	Aclonifen	1,2	Pulses	Herbicide	Boom sprayers
Lemon	Weeds	Pendimethalin	1,65	Citrus fruits +olive	Herbicide	Boom sprayers

Realistic application practices				Results for application scenarios		
Crop	**Pest or disease**	**Active ingredient**	**Dose kg_{AI} ha^{-1}**	**Crop class**	**Pesticide target**	**Application method**
Nectarine	Rust	Mancozeb	0,37	Fruits temperate	Fungicide	Air-blast sprayer
Potato	Orthoptera	Chlorpyrifos	0,08	Roots and tubers	Insecticide	Air-blast sprayer
Rice	Weeds	Bensulfuron methyl	0,06	Paddy rice	Herbicide	Boom sprayers
Spinach	Orthoptera	Chlorpyrifos	0,10	Vegetables leafy	Insecticide	Hand operated sprayers
Tomato	Mildew	Mancozeb	0,37	Vegetables fruit	Fungicide	Air-blast sprayer
Wheat	Weeds	Pendimethalin	1,65	Pooideae	Herbicide	Boom sprayers

With these results is possible to infer that the application scenarios defined are a significant input, which can capture some of the most relevant features of pesticide application practices, to quantify default pesticide emission fractions for use in LCA.

4.4 Conclusions

The application scenarios defined capture the critical factors for determining pesticide distribution in a representative variety of cropping systems. The main strength of these developed scenarios is the transparency and open development in every step of the process, comprising the acceptance of different stakeholders and the scientific support of experts involved in the consensus effort.

Finally, this combination of likely application scenarios represents one-step towards the consensus to estimate global emission fractions of pesticides. For practitioners, these results constitute a simplification and an advance for been able to compare different agricultural practices in the context of pesticide use assessment in LCA studies. Further developments should include efforts to improve application method aggregation and the inclusion when possible of different categories such as soil disinfection and seed dressing; other crop classes such as flower crops, Bromeliaceae (e.g., pineapple), and to test the effects of the adjuvants on pesticides to quantify emission fractions.

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Chapter 5.

General conclusions and Outlook

5.1 General conclusions

In this thesis, the methodologies to quantify emission fractions, toxicity impacts on ecosystems and define pesticide application scenarios were advanced to facilitate the assessment of pesticides use in open-field crop production.

The ecotoxicological burden on freshwater ecosystems from pesticide use was evaluated by using Denmark´s feed production from the period 2013- 2015 as a case of study. Besides, the influence of the emission inventory modeling on the environmental impact profiles of maize, grass, winter wheat, spring barley, rapeseed and peas was assessed. At the same time, a simplified estimation routine that allows the inclusion of the agricultural field on the assessment for pesticide emission fractions was proposed. Furthermore, it was framed a suitable interface for pesticide emission inventory (LCI) and impact assessment (LCIA) and the related mass distribution of pesticide avoiding a temporal overlapping. Freshwater impacts did not follow the same trend and did not present any direct correlation to the pesticide amount applied. Some of the main factors influencing impact results were the interface between inventory estimates and impact assessment, and the consideration of when (i.e. crop growth development) and how pesticides are applied (i.e. application method or equipment).

Freshwater and soil ecotoxicity impacts of copper-based fungicides were quantified and characterized including spatial differentiation on the assessment in a practical case study on European vineyard production to improve the considerations of metal-based pesticides in ecotoxicity impact assessment of agricultural production. The consistent use of soil and water chemistry values has proven to be particularly important in the ecotoxicity impact evaluation of copper-based fungicides. Furthermore, the inclusion of ecotoxicity impacts of metal-based pesticides provided valuable additional insight into the environmental performance of different agricultural systems, especially for organic crop production. Hence, improving the accuracy and reliability of environmental impact profiles of cropping systems allowing at the same time, more realistic comparisons.

5. 2 Limitations and practical relevance

Some of the limitations of this thesis are related to the data quality and uncertainties. In this regard the uncertainty of the methods used in this work where not measured, these measurement is beyond the scope of the present study.

The methodology applied to characterize Cu(II) do not capture important aspects of metal speciation, such as essentiality or active plant uptake. Although the translation on the LCIA is not straightforward, because specific important spatially varying characteristics, such as cation exchange capacity describing the ionic composition of soil pore water, are not routinely measured. As demonstrated by Owsianiak et al. (2013), CFs for copper are determined mainly by OC (influencing fate) and pH (influencing bioavailability). LCIA models should, therefore, be metal-specific, and the results presented here cannot be extrapolated to other metals. In this regard, the modeling framework used in this study is only applicable to non-calcareous soils, although it is acknowledged that vineyard cultivation in calcareous soils is a typical practice in many European areas.

On the other hand, the work on this thesis contributes to various practical implementations for life cycle assessment of agricultural products and systems. These include:

- The advances related to the LCI help to simplify this process, especially important for consultants, industry, and all those practitioners who need to include agricultural systems in their background process to perform an LCA study.
- The contribution of this thesis to LCA application on agricultural systems, involves assisting decision makers to understand better copper-based fungicide behavior and the importance of distinguishing its environmental impact depending on the different receiving environments and how restrictions on the use of this fungicides should take into account the emission site.
- This study has several implications for impact assessment of copper-related compounds. Considering geographic variability both in metal hazard and LCA might provide more accurate results for the evaluation of ecotoxicity impacts, and will help to draw conclusions that are more reliable in environmental impact profiles.

- The application scenarios developed in this thesis consisted of a first step for the estimation of global default pesticide emission fractions. As remarked in chapter 4, there are many influencing factors and processes affecting pesticide distribution. Therefore, these application scenarios represent the complexity and variability of agricultural practices while simplifying and facilitating the assessment of pesticide application. It is worth to mention that focusing on LCA practitioner a balanced simplification could help to consumers, industry and policymakers to deal with the environmental aspects of agricultural production, while deepening into much more elaborated methodologies with a high need of data and time consumption to assess such a complex sector could hamper its assessment.

These outcomes establish an extended vision of LCA to agricultural production, not only through ecotoxicity impact evaluation but also through the inclusion of spatially differentiated outputs and the use of emerging methodologies.

5. 3 Further research needs

The methodological advances for the ecotoxicity assessment of pesticide use are opening numerous perspectives. Furthermore, from the outcomes and conclusions of this dissertation, different possibilities for future research work are identified. These perspectives are presented below as a sort of roadmap:

a) *Account for the effect of adjuvants in pesticide formulations and chemical mixtures in the environment*

   Agricultural areas are subject of many interventions and pesticide emissions rarely take place in isolation. The environmental media is commonly exposed to different mixtures of chemicals. Accounting for the effect of these chemical mixtures and their interaction in the media may potentially increase pesticides toxicity; an example for this is the presence of surfactants, a common substance in pesticide formulation (Dollinger et al., 2018; Khan and Brown, 2016). Likewise, impacts linked to background concentrations from early applications (especially important for metal-based pesticides). Current methodologies to deal with mixture toxicity of chemicals are available and have validated for pesticides (Backhaus and Faust, 2012; Nowell et al., 2014). The challenging task now is how to integrate those with the current characterization methodologies.

b) *The inclusion of transformation products on the assessment of pesticides*

Present models lack the capabilities to account for the transformation products of pesticide active ingredients (e.g., metabolites), a possibly serious deficiency that needs further attention. This is particularly troublesome for substances that rapidly degrade into more stable compounds, some of which are more toxic than the parent one (e.g., Fosetil-Al into ethanol and phosphonic acid). According to van Zelm et al. (2010), the inclusion of such transformation products could increase (up to 5 orders of magnitude) the characterization results for freshwater ecosystems.

c) *Influence of metal emissions on impacts from agricultural production*

Advance in the assessment and further inclusion of metal emissions from agricultural production (e.g., application of pesticides, manure and chemical fertilizers) into LCA studies. Furthermore, characterizing the critical aspects (such as essentiality for plants, humans and ecosystems; bioavailability, degradability, among others) to not only consider toxicity assessment of metals in ecosystems and residues in food crops, but also to improve the consideration of metal emissions in other relevant indicators for LCA.

d) *Groundwater ecotoxicity pathways and impact characterization*

Groundwater is recognized as significant impact pathway for pesticides toxicity. Furthermore, it is an emission compartment that is not consistently linked to LCIA models. Hence, further research is needed for a groundwater ecotoxicity indicator and clear guidelines on how to use LCIA models with groundwater in combination with emissions to groundwater ecosystems.

e) *Terrestrial ecotoxicity indicator and characterization factors for soils*

Terrestrial ecotoxicity for soil organisms is a specific impact pathway or indicator that have been shown to be relevant in the context of pesticides ecotoxicity, and is commonly overlooked and not included in LCA studies involving agricultural systems. Advances for metals have been already implemented and successfully applied in the work of Owsianiak (2013) showing its importance. However, further efforts need to be conducted for terrestrial ecotoxicity characterization of pesticides and the development of terrestrial ecotoxicity as indicator.

Although research is still required to fully address ecotoxicity impacts from pesticides and other agrochemicals, this thesis has contributed to advance in the methodologies to quantify those impacts. The less significant factors involved in this assessment have been simplified without losing rigorousness. Otherwise, those significant ones to the assessment have been highlighted or included. This contribution implies a step forward in the consensus effort initiative and could be used as input for the operationalization of pesticides assessment in LCA studies.

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